Synthesis and Structural Systematics of First-Row Transition Metal Complexes with 2-[Bis(benzimidazol-2-ylmethyl)amino]ethanol

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Nickel(II) Complex, Oxovanadium(IV) Complex, X-Ray

A nickel(II) complex with (bbimae) (= 2-[bis(benzimidazol-2-ylmethyl)amino]ethanol), [Ni(bbimae)(NCS)2]•H2O (1) and an oxovanadium(IV) complex, [VO(bbimae)(NCS)2]•dma (dma = N,N-dimethylacetamide) (2) have been prepared and their crystal structures determined by X-ray diffraction. Crystal data for 1 at 293 K: a = 13.334(2), b = 17.048(2), c = 10.3829(9) Å, space group P212121, Z = 4, and dcalc = 1.41 g cm−3. Crystal data for 2 at 293 K: a = 14.099(2), b = 14.998(4), c = 14.051(2) Å, α = 107.634(9)°, space group P21/c, Z = 4, and dcalc = 1.36 g cm−3. In the nickel(II) complex, (bbimae) functions as a tetradentate ligand, and the geometry around Ni(II) ion is best described as distorted octahedral. The structure is very similar to those of the corresponding Co(II) and Mn(II) complexes. In the case of 2, which is also distorted octahedral, (bbimae) is a tetradentate ligand without the coordination of the alcohol group. The M—N (benzimidazole) bond length is 1.95–2.18 Å, and also observed for other first-row transition metal complexes with (bbimae), and differ in the order V(IV) < Mn(II) > Co(II) > Ni(II) > Cu(II), consistent with the effective ionic radii of the metal ions. Comparison of the structural parameters of these complexes with those of the metal ions in biological systems has supported the usefulness of the tripod-like ligands to synthesis model compounds for biological systems.

1. Introduction

Transition metal ions occur in metalloenzymes bound to several different donor atoms of peptide chains usually in highly distorted environments, such as found in plastocyanin, hemocyanin and hemerythrin, etc. [1—4]. There has been great deal of effort focused towards obtaining model compounds for the above metalloproteins [5—21].

In previous papers, we have reported the preparations of several metal complexes of tripod ligands in order to gain the models for copper- and non-heme iron-containing proteins [22—29]. Tripod-ligands are very suitable for the above purpose in that (a) several different kinds of ligand groups such as benzimidazole, phenol, thioether and pyridine can be included in one ligand, and (b) the environment around the metal ion in these compounds is flexible and elastic; for example the structure of [Cu(ntb)X]2+ (X = Cl, Br) are trigonal bipyramidal, whereas a square pyramidal structure has been assigned to [Cu(ntb)(imidazole)]2+ on the basis of the ESR spectra [23], where (ntb) represents tris(2-benzimidazolylmethyl)amine. These functions as models for oxyhemocyanin [22], Type-I and Type-II copper proteins [23, 27], Type-III proteins [25, 29], pyrocatechase [26], oxyhemerythrin and oxytyrosinase [28].

In the course of this work, we also found that 2-[bis(benzimidazol-2-ylmethyl)amino]ethanol (hereafter abbreviated as (bbimae)) reacts with several metal ions to give crystals suitable for X-ray analysis [30—34].

In this article we report on the preparation of the complexes [Ni(bbimae)(NCS)2]•H2O (1) and [VO(bbimae)(NCS)2]•dma (dma = N,N-dimethylacetamide) (2) and the determination of their crystal structures by X-ray diffraction method, and discuss the structural properties of first-row transition metal complexes of (bbimae) in terms of the coordination features and ionic radii of the metal ions.

* Reprint requests to Dr. Y. Nishida.

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2. Experimental

Synthesis

The ligand (bbimae) was prepared by the Nishida's method [23]. The metal complexes were obtained as follows.

$[\text{Ni(bbimae)}(\text{NCS})_2] \cdot \text{H}_2\text{O}$

To a hot methanol solution (30 ml) of (bbimae)-H$_2$O (1020 mg, 0.003 mol) was added a methanol solution (15 ml) of Ni(NO$_3$)$_2$·6H$_2$O (870 mg, 0.003 mol). An aqueous solution (25 ml) of NH$_4$NCS (530 mg, 0.007 mol) was added to this solution, and the mixture was allowed to stand for 10 days. The blue fine crystals precipitated were collected by filtration. The crude crystals (500 mg) thus obtained were dissolved in ethanol (40 ml), and water (60 ml) was added. Blue prisms were obtained after standing for a week. They were collected by filtration, and dried in vacuo over P$_2$O$_5$ for two days.

$\text{C}_{20}\text{H}_{21}\text{N}_7\text{O}_2\text{S}_2\text{Ni}$

Found C 46.83 H 4.41 N 19.22,
Calcd C 46.71 H 4.12 N 19.07.

$[\text{VO(bbimae)}(\text{NCS})_2] \cdot \text{dma}$

A hot methanol solution (30 ml) of (bbimae)-H$_2$O (1020 mg, 0.003 mol) and an aqueous solution (30 ml) of VOSO$_4$·5H$_2$O (760 mg, 0.003 mol) were mixed. To this solution was added a methanol solution (20 ml) of NH$_4$NCS (530 mg, 0.007 mol), and the mixture was allowed to stand for one day at 4 °C. The pale violet powder (50 mg) thus obtained was dissolved in dma (5 ml), and aqueous methanol (1/1 (v/v), 15 ml) was added. The solution was left to stand for a week at room temperature, and blue-violet prisms deposited. They were collected by filtration, washed with methanol, and dried in vacuo over P$_2$O$_5$ for 2 days.

$\text{C}_{20}\text{H}_{28}\text{N}_8\text{O}_5\text{S}_2\text{V}$

Found C 48.69 H 4.82 N 18.84,
Calcd C 48.73 H 4.77 N 18.94.

X-ray data collection

The crystals were mounted on a Rigaku AFC-5 four-circle automatic diffractometer. Graphite monochromated MoK$_\alpha$ radiation ($\lambda = 0.71069$ Å) was used. Automatic centering and least-squares routines were carried out on 25 reflections for each complex to obtain the cell constants given in Table I. The $\omega-2\theta$ scan technique was employed to measure the intensities for a unique set of reflections. Three check reflections were measured every 100 reflections. They exhibited no significant decay during the data collection. Intensities were corrected for Lorentz and polarization effects.

Structure solution and refinement

The structures were solved by direct methods (MULTAN 78) [35], and successive Fourier and difference-Fourier syntheses. The structures were refined by block-diagonal least-squares procedures. The

<table>
<thead>
<tr>
<th>Complex</th>
<th>$[\text{Ni(bbimae)}(\text{NCS})_2] \cdot \text{H}_2\text{O}$</th>
<th>$[\text{VO(bbimae)}(\text{NCS})_2] \cdot \text{dma}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula</td>
<td>$\text{C}<em>{20}\text{H}</em>{21}\text{N}_7\text{O}_2\text{S}_2\text{Ni}$</td>
<td>$\text{C}<em>{22}\text{H}</em>{28}\text{N}_8\text{O}_5\text{S}_2\text{V}$</td>
</tr>
<tr>
<td>M</td>
<td>514.3</td>
<td>567.6</td>
</tr>
<tr>
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<td>P2$_2_1_2_1$</td>
<td>P2$_1/c$</td>
</tr>
<tr>
<td>a [Å]</td>
<td>13.334(2)</td>
<td>14.099(2)</td>
</tr>
<tr>
<td>b [Å]</td>
<td>17.048(2)</td>
<td>14.998(4)</td>
</tr>
<tr>
<td>c [Å]</td>
<td>10.3829(9)</td>
<td>14.051(2)</td>
</tr>
<tr>
<td>$\beta$ [°]</td>
<td>90</td>
<td>107.634(9)</td>
</tr>
<tr>
<td>U [Å$^3$]</td>
<td>2360.2(5)</td>
<td>2831.5(8)</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>D$_s$ [g cm$^{-3}$]</td>
<td>1.41</td>
<td>1.36</td>
</tr>
<tr>
<td>D$_m$ [g cm$^{-3}$]</td>
<td>1.45</td>
<td>1.39</td>
</tr>
<tr>
<td>F(000)</td>
<td>1064</td>
<td>1180</td>
</tr>
<tr>
<td>Crystal dimensions [mm]</td>
<td>0.3×0.4×0.4</td>
<td>0.3×0.3×0.4</td>
</tr>
<tr>
<td>Scan rate [°] min$^{-1}$</td>
<td>6</td>
<td>6</td>
</tr>
<tr>
<td>Scan range (2θ) [°]</td>
<td>3.0–55.0</td>
<td>3.0–55.0</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>2356</td>
<td>3930</td>
</tr>
<tr>
<td>Independent reflections (&gt;3σ</td>
<td>Fo</td>
<td>)</td>
</tr>
<tr>
<td>$\mu$ (MoK$_\alpha$) [cm$^{-1}$]</td>
<td>8.61</td>
<td>5.63</td>
</tr>
</tbody>
</table>

Table I. Crystal data for 1 and 2.

| $R$ (= $\Sigma||\text{Fo}|-|\text{Fc}||/\Sigma|\text{Fo}|$) | 0.036                                           | 0.045                                           |
| $R’$ (= ($\Sigma||\text{Fo}|-|\text{Fc}||/\Sigma|\text{Fo}|)^{1/2}$) | 0.036                                           | 0.048                                           |
| Largest peak [e Å$^{-3}$] | 0.39                                               | 0.23                                           |

a Measured by floatation in $n$-C$_4$H$_8$/BrC$_2$H$_5$/CH$_4$/Br;

b largest peak in the final difference-Fourier map.
reliability indices refer to \( R = \frac{\sum |F_o| - |F_c|}{\sum |F_o|} \) and \( R' = \frac{\sum (|F_o| - |F_c|)^2}{\sum |F_o|^2} \). The positions of H-atoms were determined from the difference-Fourier maps based on the refined non-H-atoms. In the final refinement, 21 and 17 H-atoms were included with isotropic thermal parameters for \( 1 \) and \( 2 \), respectively. The final shifts of the atomic parameters of non-H-atoms were less than 0.3 times their estimated standard deviations. All the calculations were performed on a Facom M-200 computer by the local version [36] of UNICS II [37] and ORTEP [38] programs. The thermal ellipsoids of the ORTEP plots were drawn at 50% probability level. The atomic scattering factors of non-H-atoms were taken from ref. [39], and those of H-atoms were adopted from the Tables of Stewart et al. [40]*.

Infrared Spectra

Infrared spectra were recorded by a Hitachi-Perkin Elmer Grating Infrared Spectrophotometer model 225 on a KBr disk.

3. Results and Discussion

Molecular structure of \( 1 \)

Compound \( 1 \) crystallizes in the orthorhombic space group \( P_{2_1}2_12_1 \). The final atomic parameters are listed in Table II, and the important bond distances and angles in Table III. As shown in Fig. 1, the (bbimae) functions as a tetradentate ligand in this complex, and the geometry around the nickel(II) ion is best described as a distorted octahedron. This structure is very similar to those of the corresponding cobalt(II) and manganese(II) complexes [31, 34].

The coordination bond lengths and the deviation of the equatorial atom from the best-fit planes generally decrease in the order Mn(II) > Co(II) > Ni(II). In \( 1 \), two NCS ions coordinate in the \( cis \)-form and each M–NCS bond is almost linear (deviations from 180° are in the range 6–28°). The coordination mode of (bbimae) in \( 1 \) resembles that in [Ni(tren)(NCS)\(_2\)] [41], where tren represents tris(2-aminoethyl)amine. The two benzimidazole planes of (bbimae) are nearly parallel, the dihedral angle being 7.8°.

The intermolecular contacts in \( 1 \) are different from those of the Co(II) and Mn(II) complexes due to the presence of the lattice water (cf. Table IV). The contacts less than 3 Å in Table IV imply the presence of hydrogen bonds. The S(A)–O(W) contacts (ca. 3.2 Å, Table II. Atomic co-ordinates (\( \times 10^4 \)) for \( 1 \) with estimated standard deviations in parentheses.

<table>
<thead>
<tr>
<th>Atom</th>
<th>( x )</th>
<th>( y )</th>
<th>( z )</th>
</tr>
</thead>
<tbody>
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<td>8519(3)</td>
<td>1174(3)</td>
<td>475(5)</td>
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<td>9349(4)</td>
<td>1096(3)</td>
<td>163(5)</td>
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<td>10534(1)</td>
<td>1022(1)</td>
<td>-259(2)</td>
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<tr>
<td>N(B)</td>
<td>6731(4)</td>
<td>1510(3)</td>
<td>2205(4)</td>
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<tr>
<td>C(B)</td>
<td>6407(4)</td>
<td>1376(3)</td>
<td>3200(5)</td>
</tr>
<tr>
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<td>6573(3)</td>
<td>618(2)</td>
<td>-418(4)</td>
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<td>N(2)</td>
<td>6594(4)</td>
<td>-175(3)</td>
<td>-2100(5)</td>
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<td>C(1)</td>
<td>6863(4)</td>
<td>527(3)</td>
<td>-1614(5)</td>
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<td>6079(4)</td>
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<td>-109(5)</td>
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<td>C(3)</td>
<td>5580(4)</td>
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<td>1023(6)</td>
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<td>1055(7)</td>
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<td>C(7)</td>
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<td>N(3)</td>
<td>7704(3)</td>
<td>2763(2)</td>
<td>422(4)</td>
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<td>C(8)</td>
<td>8063(4)</td>
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<td>C(9)</td>
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<td>C(10)</td>
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<td>C(11)</td>
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<td>4159(4)</td>
<td>3154(6)</td>
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<td>C(12)</td>
<td>8343(5)</td>
<td>4780(4)</td>
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<td>C(13)</td>
<td>8526(5)</td>
<td>4730(4)</td>
<td>1145(7)</td>
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<td>C(14)</td>
<td>8283(4)</td>
<td>4023(3)</td>
<td>575(6)</td>
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<td>7254(3)</td>
<td>1918(3)</td>
<td>-1704(4)</td>
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<td>1144(4)</td>
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<td>C(16)</td>
<td>8109(4)</td>
<td>2458(3)</td>
<td>-1837(3)</td>
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<td>C(17)</td>
<td>6315(4)</td>
<td>2512(4)</td>
<td>-2149(5)</td>
</tr>
<tr>
<td>C(18)</td>
<td>5407(4)</td>
<td>2038(4)</td>
<td>-1385(6)</td>
</tr>
<tr>
<td>O</td>
<td>5611(3)</td>
<td>2122(2)</td>
<td>18(3)</td>
</tr>
<tr>
<td>O(W)</td>
<td>3833(4)</td>
<td>736(3)</td>
<td>3179(5)</td>
</tr>
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* Complete tables of atomic coordinates and anisotropic thermal parameters and observed and calculated structural factor amplitudes have been deposited at the Fachinformationszentrum Energie, Physik, Mathematik GmbH, D-7514 Eggenstein-Leopoldshafen 2. The Registry-Nr., CSD, the name of the author, and the reference should be given.

Fig. 1. ORTEP drawing of [Ni(bbimae)(NCS)\(_2\)].
Table III. Selected bond distances (Å) and angles (°) of the co-ordination spheres in 1 and 2 with their estimated standard deviations in parentheses.

<table>
<thead>
<tr>
<th>Complex 1</th>
<th>Complex 2</th>
</tr>
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<tbody>
<tr>
<td>Ni—N(A)</td>
<td>V—N(A)</td>
</tr>
<tr>
<td>Ni—N(B)</td>
<td>V—N(B)</td>
</tr>
<tr>
<td>Ni—N(1)</td>
<td>V—N(1)</td>
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<td>V—N(3)</td>
</tr>
<tr>
<td>Ni—N(5)</td>
<td>V—N(5)</td>
</tr>
<tr>
<td>Ni—O</td>
<td>V—O(V)</td>
</tr>
<tr>
<td>N(A)—C(A)</td>
<td>N(A)—C(A)</td>
</tr>
<tr>
<td>C(A)—S(A)</td>
<td>C(A)—S(A)</td>
</tr>
<tr>
<td>N(B)—C(B)</td>
<td>N(B)—C(B)</td>
</tr>
<tr>
<td>C(B)—S(B)</td>
<td>C(B)—S(B)</td>
</tr>
</tbody>
</table>

Table IV. Intermolecular contact distances in [M(bbimae)(NCS)₂] (M = Co(II), Ni(II), and Mn(II)) complexes.

(A) Contact distances (<3.5 Å)

<table>
<thead>
<tr>
<th>Metal ion</th>
<th>Contact Distance [Å]</th>
<th>Symmetry code of the atom (ii)</th>
</tr>
</thead>
<tbody>
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<td>Mn(II)</td>
<td>N(2)—O</td>
<td>2.925(7) 1/2—x, −y, z—1/2</td>
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<tr>
<td></td>
<td>S(A)—O</td>
<td>3.170(5) −x, 1/2+y, 1/2−z</td>
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<tr>
<td></td>
<td>C(A)—S(B)</td>
<td>3.480(7) x, y, z=1</td>
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<tr>
<td></td>
<td>N(A)—S(B)</td>
<td>3.487(7) x, y, z=1</td>
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<tr>
<td>Co(II)</td>
<td>N(4)—O</td>
<td>2.968(7) 1/2—x, −y, z—1/2</td>
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<td></td>
<td>S(A)—O</td>
<td>3.154(5) −x, 1/2−y, −z</td>
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<td></td>
<td>C(A)—S(B)</td>
<td>3.497(7) x, y, z=1</td>
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<td></td>
<td>N(A)—S(B)</td>
<td>3.509(7) x, y, z=1</td>
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<tr>
<td>Ni(II)</td>
<td>O(W)—N(4)</td>
<td>2.801(7) 1/2—x, 1/2−y, −z</td>
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<td>(O(W)—H(N(4))</td>
<td>1.88(9) 1/2—x, 1/2−y, −z</td>
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(B) Hydrogen bonding in 1

<table>
<thead>
<tr>
<th>Bond L—M</th>
<th>Distance [Å]</th>
<th>Symmetry code of atom M</th>
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</thead>
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<td>N(2)—O(12)</td>
<td>2.976(5)</td>
<td>1−x, −y, −z</td>
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<tr>
<td>H(N(2))—O(12)</td>
<td>1.97(5)</td>
<td>1−x, −y, −z</td>
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<tr>
<td>N(4)—O(12)</td>
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<td>H(N(4))—O(12)</td>
<td>2.09(5)</td>
<td>1/2−x, 1/2−y, 1/2−z</td>
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</table>

* (i) and (ii) denote the neighboring two molecules.

Molecular structure of 2

Compound 2 crystallizes in the monoclinic space group P2₁/c. The final atomic coordinates and the selected bond distances and angles are given in Table V and III, respectively. Fig. 2 shows that the (bbimae) functions as a tridentate ligand and that the alcohol oxygen atom does not coordinate to the V(IV) ion. The coordinate geometry around V(IV) ion can be described as an octahedron with a consid-
Table V. Atomic co-ordinates (×10^4) for 2 with estimated standard deviations in parentheses.

<table>
<thead>
<tr>
<th>Atom</th>
<th>x</th>
<th>y</th>
<th>z</th>
</tr>
</thead>
<tbody>
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<td>4048(3)</td>
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<td>5451(10)</td>
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</table>

There is considerable distortion along the axis through O(1), V, and N(5). The nitrogen atoms of the two NCS ions (N(A) and N(B)) and two benzimidazoles (N(1) and N(3)) coordinate to the V(IV) ion in the cis-form, forming the equatorial part. The deviation of the V(IV) ion (0.37 Å) from the equatorial plane towards O(1) falls in the range of those reported for octahedral complexes (0.26–0.41 Å) [43, 44]. The V=O distance (V=O(1), 1.580 Å) is the shortest among related complexes (1.58–1.63 Å) [43, 44], and almost the same as that in the five-coordinated square pyramidal complex [VO(phthalocyanin)] (1.580 Å) [45]. The V-N(5) bond distance (2.525 Å) trans to V=O is quite long and is out of the range of those in octahedral complexes (2.1–2.3 Å), consistent with the short V=O distance. Both of V-NCS bonds are roughly linear.

Infrared spectra

In the infrared spectrum of (2), v(V=O) was observed at 989 cm⁻¹ (cf. Fig. 3), which is in-between v(V=O) of five-coordinate (>990 cm⁻¹) and six-coordinate (<990 cm⁻¹) V(IV)=O complexes [43, 44].

Comparison of structural features of first-row transition metal complexes of (bbimae)

The structural data of first-row transition metal complexes of (bbimae) are summarized in Table VI, and their features illustrated in Fig. 4.

The bond lengths of metal-benzimidazole nitrogen (M=N(1) and M=N(3)) are in the range 1.95–2.18 Å, and may be regarded as normal coordination bond distances. In spite of the structures in this series, the increasing order of these bond lengths is

![Infrared spectrum](image-url)
Table VI. Structural data and effective ionic radii of metal ions of $[\text{M(bbimae)}(\text{NCS})_2]$ ($\text{M} = \text{V}^{\text{IV}}, \text{Mn}^{\text{II}}, \text{Co}^{\text{II}}, \text{Ni}^{\text{II}}$ and $\text{Zn}^{\text{II}}$) and $[\text{Cu(bbimae)}X\text{ClO}_4]$ ($X = \text{Cl}$ or $\text{Br}$).

<table>
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<tr>
<th>Metal ion (M)</th>
<th>V(IV)O</th>
<th>Mn(II)</th>
<th>Co(II)</th>
<th>Ni(II)</th>
<th>Cu(II)</th>
<th>Zn(II)</th>
</tr>
</thead>
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<tr>
<td>Co-ordination number</td>
<td>6</td>
<td>6</td>
<td>6</td>
<td>6</td>
<td>5</td>
<td>4</td>
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<tr>
<td>Donor set</td>
<td>$\text{N}_2\text{O}_1$</td>
<td>$\text{N}_2\text{O}_1$</td>
<td>$\text{N}_2\text{O}_1$</td>
<td>$\text{N}_2\text{O}_1$</td>
<td>$\text{N}_2\text{O}_1\text{Cl}_1$</td>
<td>$\text{N}_2\text{O}_1\text{Br}_1$</td>
</tr>
<tr>
<td>Coordination geometry</td>
<td>distorted octahedron</td>
<td>distorted octahedron</td>
<td>distorted octahedron</td>
<td>distorted octahedron</td>
<td>square pyramid</td>
<td>d-TD*</td>
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<tr>
<td>Coord. bond length [Å]</td>
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<tr>
<td>M–N(1)</td>
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<td>2.06</td>
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<td>2.09</td>
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<td>M–N(5)</td>
<td>2.53</td>
<td>2.52</td>
<td>2.30</td>
<td>2.19</td>
<td>2.13</td>
<td>2.12</td>
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<tr>
<td>M–O</td>
<td>–</td>
<td>2.40</td>
<td>2.26</td>
<td>2.15</td>
<td>2.41</td>
<td>2.42</td>
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<tr>
<td>M–N(A)b</td>
<td>2.04</td>
<td>2.14</td>
<td>2.09</td>
<td>2.09</td>
<td>–</td>
<td>–</td>
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<tr>
<td>M–N(B)b</td>
<td>2.02</td>
<td>2.11</td>
<td>2.04</td>
<td>2.00</td>
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<td>–</td>
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<tr>
<td>V–O(oxo)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Cu–Cl</td>
<td>Cu–Br</td>
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<tr>
<td>E. I. R. [Å]</td>
<td>0.59</td>
<td>0.82</td>
<td>0.74</td>
<td>0.70</td>
<td>Cu–Cl</td>
<td>Cu–Br</td>
</tr>
</tbody>
</table>

* d-TD = distorted tetrahedron; b nitrogen atom of NCS ion; c effective ionic radii of metal ion taken from ref. [46].

lengths, $\text{V}^{\text{IV}}=\text{O} < \text{Mn}^{\text{II}} > \text{Co}^{\text{II}} > \text{Ni}^{\text{II}} > \text{Cu}^{\text{II}} < \text{Zn}^{\text{II}}$, are almost the same as those of the effective ionic radii of these metal ions [46], except for the case of the $\text{V}^{\text{IV}}=\text{O}$ complex (cf. Table VI).

The order of the bond distances $\text{M}–\text{N}(5)$ (tertiary amine nitrogen) is $\text{V}^{\text{IV}}=\text{O} > \text{Mn}^{\text{II}} > \text{Co}^{\text{II}} > \text{Ni}^{\text{II}} > \text{Cu}^{\text{II}} < \text{Zn}^{\text{II}}$. This is, except for the $\text{V}^{\text{IV}}=\text{O}$ complex, also the same as that of the effective ionic radii. In the case of the $\text{Zn}^{\text{II}}$ complex, the $\text{Zn}^{\text{II}}–\text{N}(5)$ distance (2.65 Å) is very long. This

![Fig. 4. Illustrations of structures of first-row transitionmetal ions. (A) $[\text{M(bbimae)}(\text{NCS})_2]$ ($\text{M} = \text{Co}^{\text{II}}, \text{Ni}^{\text{II}}, \text{Mn}^{\text{II}}$). (B) $[\text{Zn(bbimae)}(\text{NCS})_2]$. (C) $[\text{VO(bbimae)}(\text{NCS})_2]$. (D) $[\text{Cu(bbimae)}\text{X}^+ \text{(X = Cl or Br)}]$. (E) $[\text{Fe}_2\text{O(bbimae)}\text{X}_2]^2$ (X = Cl, NCS). (F) $[\text{Fe}_2(\text{bbimae}')_2(\text{NO}_3)_2]^{2+}$ (bbimae' denotes anion of (bbimae) molecule).]


may be due to the fact that the Zn(II) ion has a tendency to take on a tetrahedral coordination. In fact, the coordination geometry may be regarded as a tetrahedron if the Zn(II)—N(5) bond is neglected.

The M—O (alcohol oxygen) bond lengths of the Mn(II), Co(II) and Ni(II) complexes show the same tendency as that observed for the M—N(5) bonds. However, in the case of the copper(II) complexes, the Cu—O bonds are longer than those of the Mn(II), Co(II) and Ni(II) complexes.

**Structural comparison between model compounds and those in biological systems**

It is well known that imidazole (histidine) plays an important role in the coordination of metals at the active sites of numerous metalloproteins. Metal-imidazole binding is observed for hemocyanin, superoxide dismutase, and hemerythrin, etc.

The bond distances (M—N (imidazole)) are summarized in Table VII. In the copper proteins, Cu—N (imidazole) bond lengths are in the range 2.0—2.1 Å, very close to those observed for model compounds of tripod-ligands [8, 30]. The Fe—N (imidazol) distances are 2.2 Å (average value) in methemerythrin. Average Fe—N (benzimidazole) bond lengths are 2.03 and 2.10 Å for μ-alkoxo and μ-oxo binuclear complexes of (bbimae), respectively. These facts are supporting the usefulness of tripod-ligands for the synthesis of model compounds for copper- and non-heme iron-containing proteins.

| Table VII. Metal-imidazole bond distances in biological systems. |
|-----------------------------|--|--|
|                            | M  | distances [Å] |
| Plastocyanin                | Cu(II) | 2.07 |
| Superoxidedismutase         | Cu(II) | 2.1 |
| Amine oxidase               | Cu(II) | 1.99 |
| Methemerythrin              | Fe(III) | 2.20 |
