The Coordination Chemistry of Phosphoryl Compounds Containing the $-\text{N} (\text{CH}_3) _2$ Group, Part XI

 Complexes of Bismethyl-imido-triphosphoric-acid-pentakis-dimethyl-amide (TRIPA), a New Tridentate Ligand

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TRIPA, coordination chemistry, phosphoryl compounds

A number of new complexes containing TRIPA, chemical formula $[(\text{CH}_3) _2\text{N}]_2\text{P(O)}(\text{N}(\text{CH}_3)_2\text{P}(\text{O}))\{\text{N}((\text{CH}_3)_2\text{N})(\text{N}(\text{CH}_3)_2\text{P}(\text{O}))\{\text{N}((\text{CH}_3)_2\text{N})(\text{N}(\text{CH}_3)_2\text{P}(\text{O}))\}^n$ are reported. The compounds have the general formula $M(\text{TRIPA})_n(\text{anion})_p$, where $M = \text{Mg}, \text{Ca}, \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}, \text{Zn}, \text{Cu}, \text{Cd}$ ($p = 2$) and $\text{Al}, \text{Fe}$ ($p = 3$), $n = 1, 2$, and anion stands for $\text{BF}_4^-$, $[\text{B}(\text{C}_6\text{H}_5)_4]^-$, $\text{NO}_3^-$ and $\text{Cl}^-$. They are characterized and identified by chemical analysis and physical measurements.

It is shown that the bis-compounds contain octahedrally solvated metal ions, the ligand acting as a tridentate phosphoryl donor. Electron paramagnetic resonance measurements show some distortion of the octahedrons. The mono-compounds with the nitrate anion probably possess a five-coordinated structure whereas the chloride complexes are probably dimeric.

The occurrence of more than one geometric isomer for the group $[M(\text{TRIPA})]_2^p$ is discussed. It is concluded that the $s$-facial and $u$-facial isomers may occur; a possible connection with the size of the metal ions is indicated. The $\text{mer}$ form is rejected because of steric requirements.

Tridentate ligands of the form $A - A - A$, where $A$ is the coordinating atom, are relatively rare in coordination chemistry. With nitrogen as the donor atom $A$, an example is diethylenetriamine (dien).

The three possible geometric isomers of the complexes $[\text{Co(dien)}]_2X_4$ ($X = \text{Cr}, \text{Br}, \text{I}$) were recently reported. The optical isomers of the $\text{mer}$ and $u$-facial forms were resolved by means of column chromatography.

In a recent set of papers we studied the coordination chemistry of hexamethylphosphoramide (HMPA) and nonamethylimidodiphosphoramide (NIPA). Since NIPA (which can be looked upon as consisting of two "fused" HMPA molecules) showed an unusual tendency to form solvated metal ions, it seemed interesting to study the coordination chemistry, and especially the solvating properties, of TRIPA (which can be looked upon as consisting of three "fused" HMPA molecules).

The present paper therefore describes the preparation and identification of a number of TRIPA complexes. As far as we know, no solvates of a neutral tridentate oxygen donor have been reported in the literature.

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Experimental part

Starting materials

Most metal salts were commercially available (as hydrates) or were prepared by standard procedures. The preparation of TRIPA will shortly be published.

Preparation of the complexes

The hydrated metal salt was dissolved in acetone and trimethyl orthoformate was added (for dehydration). The ligand was added in a solution in A.R. grade acetone. Upon standing, crystals of the complexes appeared, in a few cases only after concentration of the solution or after addition of some dry diethyl ether. The crystals were filtered, washed with dry diethyl ether and finally dried in vacuo at room temperature.

Changing the solvent to methanol or methyl cyanide, or changing the metal salt to ligand ratio (from 1:1 to 1:2, or vice versa) did not influence the results.

The tetraphenylborate complex was prepared by adding a solution of $\text{NaB}(\text{C}_6\text{H}_5)_4$ in A.R. grade acetone to a solution of $\text{Co(TRIPA)}_2(\text{BF}_4)_2$ in A.R. grade acetone (in the ratio 2:1).

Most of the complexes are hydroscopic and must be handled in a dried glove-box.

Measurements

Semi-micro metal analyses were carried out by complexometric titrations. Infrared spectra were recorded on a Unicam SP 1200 (4000–400 cm$^{-1}$) and a Hi-
at the EPI-L (700 — 200 cm\(^{-1}\)) spectrophotometer, using nujol mulls sandwiched between potassium bromide and polythene windows. Ligand-field spectra of the solid compounds were obtained with a Beckman DK-2A ratio recording spectrophotometer, using magnesium oxide as a reference, in the 325 — 2500 nm region. X-ray powder diagrams were obtained with a Guinier type powder camera using Cu-K\(\alpha\) radiation. The samples were mounted with vaseline and protected from atmospheric vapour by adhesive tape. Conductivity measurements were carried out with a Philips cell, type GM 4221, and a Philips conductivity bridge, type 4249. Electron paramagnetic resonance measurements were performed on a Varian E-3 apparatus using X-band frequencies. The spectra of the powdered solid compounds were run as the first derivative. Galvanoxyl was used as a reference compound.

**Results**

**General**

In Table I the coordination compounds concerning the present work are listed together with their analytical results, colours and melting points. Further in this Table the X-ray types for the several compounds are indicated by the symbols A — C. The division into these groups was made according to the X-ray powder diagrams of the compounds, which were very similar in \(d(\AA)\) values and intensities for members of the same group. The differences in line patterns for the compounds marked with an accent and the unmarked ones are only very small. These similarities in X-ray powder patterns strongly suggest isomorphism between the several compounds of the same group.

In Table II the conductivities of some complexes in methyl cyanide are listed. The data for the bis-complexes correspond to those for 1:2 electrolytes and the data for the mono-complexes correspond to those for 1:1 electrolytes.

<table>
<thead>
<tr>
<th>Compound</th>
<th>(A_m) (cm^2\Omega^{-1}) mol(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn(TRIPA)(\text{BF}_4)_2</td>
<td>325</td>
</tr>
<tr>
<td>Cd(TRIPA)(\text{BF}_4)_2</td>
<td>260</td>
</tr>
<tr>
<td>Mg(TRIPA)(\text{NO}_3)_2</td>
<td>315</td>
</tr>
<tr>
<td>Mn(TRIPA)(\text{NO}_3)_2</td>
<td>150</td>
</tr>
<tr>
<td>Cu(TRIPA)(\text{NO}_3)_2</td>
<td>115</td>
</tr>
<tr>
<td>Zn(TRIPA)(\text{NO}_3)_2</td>
<td>134</td>
</tr>
<tr>
<td>Cd(TRIPA)(\text{NO}_3)_2</td>
<td>100</td>
</tr>
</tbody>
</table>

**Infrared spectra**

The phosphoryl stretching and bending vibrations for the free ligand are found at 1226 and 502 cm\(^{-1}\), respectively. In the complexes, these frequencies are shifted to lower and higher energy, respectively.

**Table I. Complexes of TRIPA: analyses, colours, melting points and X-ray types.**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Metal [%] found</th>
<th>Metal [%] calced</th>
<th>Colour</th>
<th>Melting point [°C]</th>
<th>X-ray type</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca(TRIPA)(\text{BF}_4)_2</td>
<td>3.89</td>
<td>3.81</td>
<td>white</td>
<td>198 — 200</td>
<td>A</td>
</tr>
<tr>
<td>Mn(TRIPA)(\text{BF}_4)_2</td>
<td>4.90</td>
<td>5.15</td>
<td>white</td>
<td>161 — 163</td>
<td>A</td>
</tr>
<tr>
<td>Fe(TRIPA)(\text{BF}_4)_2</td>
<td>5.33</td>
<td>5.22</td>
<td>cream</td>
<td>136 — 138</td>
<td>B</td>
</tr>
<tr>
<td>Co(TRIPA)(\text{BF}_4)_2</td>
<td>5.45</td>
<td>5.50</td>
<td>pink</td>
<td>216 — 218</td>
<td>B</td>
</tr>
<tr>
<td>Ni(TRIPA)(\text{BF}_4)_2</td>
<td>5.55</td>
<td>5.48</td>
<td>yellow-green</td>
<td>194 — 195</td>
<td>B</td>
</tr>
<tr>
<td>Cu(TRIPA)(\text{BF}_4)_2</td>
<td>6.07</td>
<td>5.91</td>
<td>blue-green</td>
<td>119 — 120</td>
<td>A’</td>
</tr>
<tr>
<td>Zn(TRIPA)(\text{BF}_4)_2</td>
<td>6.00</td>
<td>6.07</td>
<td>white</td>
<td>200 — 202</td>
<td>B</td>
</tr>
<tr>
<td>Cd(TRIPA)(\text{BF}_4)_2</td>
<td>10.1</td>
<td>9.99</td>
<td>white</td>
<td>207 dec.</td>
<td>A</td>
</tr>
<tr>
<td>Mg(TRIPA)(\text{NO}_3)_2</td>
<td>2.51</td>
<td>2.46</td>
<td>pink</td>
<td>199 — 201</td>
<td>—</td>
</tr>
<tr>
<td>Ca(TRIPA)(\text{NO}_3)_2</td>
<td>6.78</td>
<td>6.87</td>
<td>white</td>
<td>133 — 135</td>
<td>—</td>
</tr>
<tr>
<td>Mn(TRIPA)(\text{NO}_3)_2</td>
<td>8.95</td>
<td>9.18</td>
<td>white</td>
<td>174 — 176</td>
<td>—</td>
</tr>
<tr>
<td>Co(TRIPA)(\text{NO}_3)_2</td>
<td>5.85</td>
<td>5.77</td>
<td>light violet</td>
<td>120 — 122</td>
<td>B</td>
</tr>
<tr>
<td>Ni(TRIPA)(\text{NO}_3)_2</td>
<td>5.77</td>
<td>5.74</td>
<td>yellow-green</td>
<td>169 — 170</td>
<td>B</td>
</tr>
<tr>
<td>Cu(TRIPA)(\text{NO}_3)_2</td>
<td>10.4</td>
<td>10.5</td>
<td>blue</td>
<td>170 — 171</td>
<td>—</td>
</tr>
<tr>
<td>Zn(TRIPA)(\text{NO}_3)_2</td>
<td>10.7</td>
<td>10.7</td>
<td>white</td>
<td>99 — 102</td>
<td>—</td>
</tr>
<tr>
<td>Cd(TRIPA)(\text{NO}_3)_2</td>
<td>16.9</td>
<td>17.1</td>
<td>white</td>
<td>137 — 139</td>
<td>—</td>
</tr>
<tr>
<td>Al(TRIPA)(\text{NO}_3)_2</td>
<td>2.63</td>
<td>2.57</td>
<td>white</td>
<td>217 dec.</td>
<td>—</td>
</tr>
<tr>
<td>Fe(TRIPA)(\text{NO}_3)_2</td>
<td>5.25</td>
<td>5.17</td>
<td>yellow</td>
<td>60 — 65</td>
<td>—</td>
</tr>
<tr>
<td>Co(TRIPA)(\text{Cl}_2)</td>
<td>10.8</td>
<td>10.7</td>
<td>blue</td>
<td>182 — 184</td>
<td>C</td>
</tr>
<tr>
<td>Ni(TRIPA)(\text{Cl}_2)</td>
<td>10.6</td>
<td>10.7</td>
<td>blue-green</td>
<td>196 — 198</td>
<td>C’</td>
</tr>
</tbody>
</table>

— denotes a type different from any other.
indicating that coordination has occurred via the oxygen atoms of the ligand \(^3, 4, 10, 16\).

It is well known that infrared spectra of BF\(_4^-\) and NO\(_3^-\) ions can provide evidence about coordination to metal ions, since lowering of the symmetry dramatically influences the number of infrared absorptions \(^10, 16\). As regards the BF\(_4^-\) complexes of TRIPA, no signs of symmetry lowering were found; all compounds showed a strong band at \(^\sim 1050\) cm\(^{-1}\), due to the \(v_3\) mode of the BF\(_4^-\) ion \(^10\).

The infrared absorptions of the nitrate ions that are not masked by ligand absorptions, are listed in Table III. As can be seen from this Table, the bisco-compounds showed only one absorption for the \(v_3\) mode and a very weak absorption for the \(v_1\) mode. This indicates uncoordinated nitrate ions in these complexes \(^10, 16\). The spectra of the mono-compounds, however, are in agreement with coordinated nitrate ions \(^10, 16\).

The chloride complexes showed strong absorptions at 285 (Co\(^{2+}\)) and 290 (Ni\(^{2+}\)) cm\(^{-1}\). These bands can be attributed to the \(v_3\) mode of the (MC\(_14\))\(^2-\) anions (see also below) \(^10\).

Finally, it is remarked that the trivalent nitrate complexes showed strong absorptions at 570 and 650 cm\(^{-1}\) (Al\(^{3+}\)), and 550 cm\(^{-1}\) (Fe\(^{3+}\)), which could not be attributed to ligand or anion modes. In view of the results found for the corresponding NIPA complexes, we assign these bands to metal-ligand stretching vibrations \(^5-7, 10\). In agreement with earlier results, no signs of such bands were found in the case of the bivalent complexes \(^4-7, 10\).

**Ligand-field spectra**

For evidence about the coordination around the metal ions, and the ligand-field strength of TRIPA, reflectance spectra of the solid compounds of Fe\((II)\), Co\((II)\), Ni\((II)\), and Cu\((II)\) were taken. In Table IV the band maxima, assignments and calculated values of the ligand-field parameters \(Dq\), \(B\), \(Dq/B\) and \(\beta\) are given. Assignments and calculations are in accordance with refs. \(^17-25\).

The absorption bands for the compounds M(TRIPA)\(_2\) (anion)\(_2\), where M = Fe\((II)\), Co\((II)\), Ni\((II)\), and anion stands for BF\(_4^-\), NO\(_3^-\) and [B(C\(_6\)H\(_5\))\(_4\)]\(^-\), correspond with an octahedral environment of the metal ions \(^17-19\). The band maxima

<table>
<thead>
<tr>
<th>Compound</th>
<th>Band maxima and assignments</th>
<th>(Dq^*)</th>
<th>(B^*)</th>
<th>(Dq/B^<em>) (\beta^{</em>,\dagger})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni(TRIPA)(_2)(BF(_4))(_2)</td>
<td>7.69</td>
<td>7.22</td>
<td>13.1</td>
<td>13.1</td>
</tr>
<tr>
<td>Ni(TRIPA)(_2)(NO(_3))(_2)</td>
<td>7.69</td>
<td>7.22</td>
<td>13.1</td>
<td>13.1</td>
</tr>
<tr>
<td>Ni(TRIPA)Cl(_2)</td>
<td>7.69</td>
<td>7.22</td>
<td>13.1</td>
<td>13.1</td>
</tr>
<tr>
<td>Co(TRIPA)(_2)(BF(_4))(_2)</td>
<td>7.19</td>
<td>7.20</td>
<td>7.19</td>
<td>7.19</td>
</tr>
<tr>
<td>Co(TRIPA)(_2)(NO(_3))(_2)</td>
<td>7.19</td>
<td>7.20</td>
<td>7.19</td>
<td>7.19</td>
</tr>
<tr>
<td>Cu(TRIPA)(_2)(BF(_4))(_2)</td>
<td>9.72</td>
<td>11.5</td>
<td>11.8</td>
<td>11.5</td>
</tr>
</tbody>
</table>

Abbreviations: sh = shoulder. \(\dagger \beta = B/B_s\); \(B_s = 971\) cm\(^{-1}\) (Co\(^{2+}\)), 1030 cm\(^{-1}\) (Ni\(^{2+}\)). * Accuracies: \(Dq\), \(B\) and \(\beta \pm 2\%\), \(Dq/B \pm 3\%\). † Masked by absorptions of the (MC\(_14\))\(^2-\) ions (see text).
for the Cu(II) complexes correspond with distorted octahedrally coordinated Cu$^{2+}$ ions.

Besides absorptions due to the moiety [M(TRIPA)$_2$]$^{2+}$, strong absorptions at 5.40 and 14.8 kK (Co$^{2+}$), and 7.27 and 14.8 kK (Ni$^{2+}$) were found in the spectra of the chloride complexes. These band maxima correspond to those reported for the anions (CoCl$_4$)$^{2-}$ and (NiCl$_4$)$^{2-}$, respectively.

**Discussion**

From the results described above, it can be concluded that all bis-complexes contain solvated metal ions. This is based on the following observations:

a) Infrared spectroscopy indicated the presence of uncoordinated anions and only coordinated phosphoryl groups.

b) Conductivity measurements indicated the presence of 1:2 electrolytes (at least in methyl cyanide solutions).

c) Ligand-field spectroscopy indicated an identical first coordination sphere for all bis-compounds of a certain metal ion.

d) X-ray powder diagrams indicated isomorphism between complexes with different anions; this strongly resembles the behaviour of the NIPA solvates.

It follows thus that we can assign a solvate structure to all bis-complexes, i.e. [M(TRIPA)$_2$]$^{n+}$ (anion$^-$)$_n$.

As regards the ligand-field parameters of TRIPA, it is remarked that TRIPA possesses a higher $Dq$ value and a lower $B$ value than NIPA. The metal-oxygen distances in the TRIPA solvates may be smaller than in the corresponding NIPA solvates.

The most typical aspect of a bis-tridentate solvate is that it can exist in three different geometric forms: the mer, s-facial and u-facial isomers. Generally speaking, they can only be resolved by structure determinations and by special optical measurements (the s-facial isomer contains a center of symmetry, the u-facial and mer forms not). However, some remarks concerning the particular isomers that may be present, can be made:

Because the complexes were obtained as crystals and because different preparations yielded compounds with identical X-ray powder patterns, it seems unlikely that isomer mixtures are present. When one builds models for the various isomers, it can be seen that the mer form is very unfavourable because of steric reasons. We may therefore exclude the possibility that this isomer occurs among our complexes.

As regards the X-ray types of the tetrafluoro-borate solvates, it is interesting to note that the larger metal ions possess a different X-ray type (type A) than the smaller metal ions (type B). It might be possible that this is connected with the presence of s-facial and u-facial isomers (compare also the results obtained for NIPA).

An electron paramagnetic resonance spectrum of pure Mn(TRIPA)$_2$(BF$_4$)$_2$ consisted of a single line near $g_{\text{eff}} = 2$; this is common for Mn(II) compounds, near $g_{\text{eff}} = 2$; this is common for Mn(II) compounds, spectra of the Zn(II) and Cd(II) dopes showed considerable hyperfine-structure; the magnitude of the hyperfine splitting constant ($A$) was found to be 95 Gs. This $A$ value is in the usual range for oxygen donor ligands coordinated to Mn(II).

Undiluted Cu(TRIPA)$_2$(BF$_4$)$_2$ yielded an asymmetric EPR spectrum with $g_{||} = 2.39$ and $g_{\perp} = 2.08$, no hyperfine structure upon $g_{||}$ was resolved. When Cu(II) was doped in the lattices of Zn(TRIPA)$_2$(BF$_4$)$_2$ and Cd(TRIPA)$_2$(BF$_4$)$_2$, the parameters were, for Zn: $g_{||} = 2.43$ and $g_{\perp} = 2.07$, for Cd: $g_{||} = 2.46$ and $g_{\perp} = 2.09$ ($A_{||} = 95$ Gs). The magnitudes of the several parameters agree with oxygen-coordinated ligands to Cu(II). For all three cases, the spectra correspond with distorted species [Cu(TRIPA)$_2$]$^{2+}$.

However, the EPR spectrum of the manganese(II) doped Cd(II) compound showed more distortion than that of the manganese(II) doped Zn(II) compound. Since the models that we built showed more irregularity in the case of the u-facial isomer, we assign this form to the Cd compound (and therefore to all complexes of X-ray type A) and the s-facial form to the Zn compound (and thus to all complexes of X-ray type B). It is however emphasized that this assignment is only tentative. A definite assignment can only be reached by structure determinations in combination with special optical measurements; studies on these subjects are currently in progress.

As regards the structures of the chloride complexes, all measurements indicated the presence of the species (MCl$_4$)$^{2-}$. The dimeric-ionic structure [M(TRIPA)$_2$]$^{2+}$ (MCl$_4$)$^{2-}$ can therefore be assigned to these complexes. With NIPA, we found a cor-
responding structure (i.e. \([\text{M(NIPA)}_3]^{2+}(\text{MC14})^{2-}\)) for the Ni(II) compound \(^4\), but with CoCl\(_2\) a tetrahedral adduct, Co(NIPA)Cl\(_4\), was obtained \(^4\). It can therefore be said that TRIPA has more solvating “power” than NIPA.

The nitrate complexes of formula M(TRIPA) \((\text{NO}_3)_2\) (the mono-compounds) present some interesting problems. With the exception of the Cd(II) complex, the infrared spectra indicated the presence of equivalent coordinated nitrato groups. However, the conductivity measurements suggested the presence of 1:1 electrolytes in methyl cyanide solution. It follows then that methyl cyanide solvation must have occurred (otherwise the measurements would contradict each other). We assume therefore that the solid compounds are non-electrolytes (see above). Because of the fact that the nitrato groups are equivalent and no uncoordinated phosphoryl groups are present (see above), the only possibility is a five-coordinated structure of the type \([\text{M(TRIPA)}(\text{NO}_3)_2]^{2+}\), with monodentate coordinated nitrato groups.

For the sake of completeness, it is remarked that a dimeric-ionic structure of the type \([\text{M(TRIPA)}(\text{NO}_3)_3]^{2+}\) \([\text{M(NO}_3)_4]^{2-}\) is ruled out by the infrared spectral measurements and, in the case of Cu(II), by its ligand-field spectrum \(^27\).

As regards the five-coordinated structure, models showed that a basically square pyramidal structure is more likely than a trigonal bipyramidal one (because of steric reasons); this is as expected for oxygen donor ligands \(^28\). Various geometric isomers are again possible.

Finally, the compound Cd(TRIPA) \((\text{NO}_3)_2\) is left. Its infrared spectrum clearly indicated the presence of non-equivalent nitrato groups. Since infrared spectroscopy cannot distinguish between monodentate and bidentate coordinated nitrato ions \(^29\) (and, in this case, one of the nitrato groups might even be ionic), the following structures are possible: octahedral \([\text{M(TRIPA)}(\text{ONO}_2)(\text{O}_2\text{NO})]^{6+}\), five-coordinated \([\text{M(TRIPA)}(\text{O}_2\text{NO})]^{6+}(\text{NO}_3)^{-}\) and tetrahedral \([\text{M(TRIPA)}(\text{ONO}_2)]^{+}(\text{NO}_3)^{-}\). Because of the size of Cd(II), the octahedral structure seems the most likely but a definite assignment cannot be made.

**Conclusions**

From the results discussed above, the following conclusions can be drawn:

1. The ligand TRIPA is a strongly coordinating agent for many metal ions, yielding solvated metal ions in many cases.
2. In all complexes investigated, TRIPA acts as a tridentate phosphoryl donor.
3. The ligand occurs somewhat above NIPA in the spectrochemical and nephelauxetic series.
4. Depending on the size of the metal ion, both \(s\)-facial and \(u\)-facial isomers seem to occur among the tetrafluoroborate solvates.

The authors are indebted to Mr. A. Van der Linden for assistance with the infrared spectra and to Mr. H. Vos for assistance with the EPR spectra. Drs. W. J. J. M. Sprangers is thanked for his advice on the preparation of the ligand and Dr. J. Reedijk for many stimulating discussions.

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\(^16\) M. W. G. de Bolster and W. L. Groeneveld, Recueil Trav. chim. 90, 687 [1971].

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\(^21\) M. W. G. de Bolster and W. L. Groeneveld, Recueil Trav. chim. 91, 171 [1972].

Halogenierungs- und Oxidationsreaktionen an Metallchelatverbindungen

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Halogenation, Metal Compounds of Acetylacetone, Salicylaldehyde, Salicylic acid methyl ester

Reactions of acetylacetonate-, salicylaldehydate- and methylsalicylate-metal compounds with oxygen, bromine and sulfurylchloride were investigated. It was found, that these reactions yield to a variety of products depending on the used central metal ion.

Abkürzungen: Acac = acetylacetonato, Sal = salicylaldehydat, Salm = methyl-salicylato, Py = Pyridin, Pip = Pipperidin, Morph = Morpholin.


Es wurden Komplexe des Acetylacets (Pentandion-2.4), Salicylaldehyds und Salicylsäuremethyl esters verschieden Halogenierungs- und Oxidationsreaktionen unterworfen und die Reaktionsbedingungen jeweils optimiert. Als Zentralmetallionen wurden sowohl dia- wie auch paramagnetische Metallionen eingesetzt, als zusätzliche Liganden in der Axialstellung der untersuchten pseudo-oktaedrischen Bis-(chelat)-metall(II)-Komplexe wurden Pyridin, Piperidin, Morpholin und Wasser verwendet.

Umsetzungen mit Sulfurylchlorid

Im folgenden sei eine Vorschrift unter optimalen Reaktionsbedingungen, vertretend für alle Umsetzungen mit Sulfurylchlorid, angegeben.

Zur 0,05 Mol Bis(acetylacetonato)-bis(piperidin) Kobalt(II), suspendiert in 75 ml BenzoI (Wassergehalt des Benzols 0,06%) wurde innerhalb von 20 Min. unter schnellem Rühren und Kühlen (Eis/Kochsalz) 0,1 Mol Sulfurylchlorid zugetropft. Die entstehende Salzsäure wurde durch die berechnete, bereits vor dem Reaktionsbeginn zugefügte Menge NaHCO₃ neutralisiert. Anschließend wurde das Benzol an der Wasserstrahlpumpe abgezogen und der Rückstand (zu Tränen reizend, ölig) ausgeäthert. Nach dem Trocknen und Abziehen des Äthers bleibt durch Acetylaceton (Pentandion-2.4) und 3-Chlor-pentandion-2.4 stark verunreinigtes 3.3-Dichlor-pentandion-2.4 zurück. Das gleiche Ergebnis wurde erhalten, wenn die Reaktion unter N₂ als Schutzgas oder bei Gegenwart eines Radikalinhibitors (Hydrochinon) durchgeführt wird.

Im Gegensatz zu der Umsetzung des freien Acetylacetons mit der äquivalenten Menge Sulfurylchlorid, die nur zur Monochlorierung des Acetylacetons führt, wird also bei Einsatz des Acetylacetonato-Komplexes das freie dichlorierte Produkt erhalten, während das sicherlich auch gebildete 3-Monochlorpentandion-2.4 komplex gebunden bleibt.

An Reaktionsbedingungen wurden variiert: die Zutropfzeit des SO₂Cl₂ (zwischen 10 und 240 Min.), die Reaktionstemperatur (sie darf 40 °C nicht überschreiten), die Lösungsmittelmengen (zwischen 50 und 500 ml für 0,05 Mol Komplex), das Neutralisationsmittel (es wurde Morpholin, K₂CO₃ und NaHCO₃ verwendet), der Wassergehalt des Lösungsmittels (zwischen 0,0 und 0,07%) und, wie bereits angeführt, der Axialligand.

Unter den oben genannten Reaktionsbedingungen wurden im Reaktionsprodukt etwa 80% 3.3-Dichlorpentandion-2.4 gefunden. Wird der Wassergehalt des Lösungsmittels Benzol um ±0,01% variiert, so sinken...