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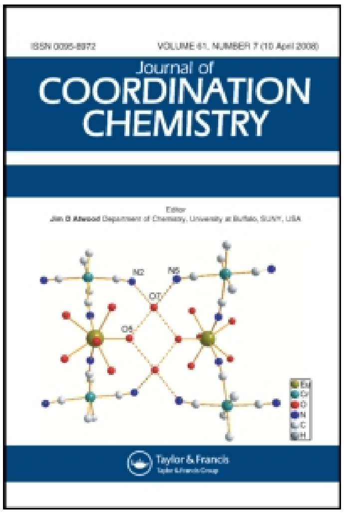

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# MACROBICYCLIC TRIS-DIOXIMATES. REACTIONS OF COBALT (III) TRIS-DIOXIMATES WITH TIN(IV) FLUORIDE AND BROMIDE

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Macrobicyclic anions of general formula $[CoD_3(SnBr_3)_2]^-$ have been produced by a template reaction on $Co^{3+}$ of differen α-dioximes ($H_2D$) and tin (IV) tetrabromide; the anions were isolated and characterized as corresponding acids or salts with organic cations. Electron density distributions in the compounds has been measured by electronic, polynuclear ($^{59}Co$, $^{119}Sn$, $^{13}C$, $^{1}H$) NMR and $^{119}Sn$ Mössbauer spectroscopy. Data have been compared with results obtained for similar tin chloride compounds and iron(II) complexes. Ligand field effects in $[CoD_3(SnBr_3)_2]^-$ anions are discussed in terms of X-ray structure data for the complex $N(n\text{-}C_4H_9)_4[CoNx_3(SnBr_3)_2]$, Nx = nioxime.

KEYWORDS: macrobicyclic complexes, electronic structure, cobalt, oximes, Mössbauer effect.

## INTRODUCTION

P-block element compounds, which are Lewis acids, can act as cross-linking agents in the encapsulation of d-metal ions (*e.g.*, iron(II), cobalt(II, III), ruthenium(II) ions) by macrobicyclic tris-dioximate ligands.[1-11] Cross-linking proceeds most effectively in the case of boron residues of general formula BR (where R is halogen, aryl, alkyl, hydroxyl, alkoxyl, ferrocenyl). The boron atoms have a tetrahedral coordination. Cross-linking with tin(IV) compounds is less effective. Only the encapsulation of iron(II) and cobalt(III) involving tin tetrachloride has been a success to the present.[2,3] In these cases, the tin atom has an octahedral coordination.

Preliminary experiments, which covered a wide range of tin compounds, led to no positive result — we did not form clathrochelate complexes. Only tin tetrabromide proved to be an effective cross-linking agent in the case of some α-dioximes; this made the present study possible.

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## EXPERIMENTAL

### *Materials*

The reagents used, $CoBr_2$, $SnBr_4$, diethylamine (DEA), dimethylglyoxime, $\alpha$-benzyldioxime, nioxime, as well as organic solvents, were obtained commercially. The other dioximes listed in Table 1 were synthesized by reported methods.[12]

### *Measurements*

Carbon, hydrogen and nitrogen contents were analysed with a Carbo Erba model 1106 microanalyser. IR spectra of solid samples (CsI pellets) in the range 200–4000 cm$^{-1}$ were recorded on a Specord M-80 spectrophotometer. Band assignments were made using results obtained earlier[1] as well as with model compounds. Electron absorption spectra of acetonitrile solutions in the range 11000–45000 cm$^{-1}$ were recorded on a Perkin Elmer Lambda 9 spectrophotometer. $^1H$, $^{13}C\{^1H\}$, $^{59}Co$ and $^{119}Sn$ NMR spectra of acetone-$d_6$ and $CD_3CN$ solutions were obtained on a Bruker CXP-200 spectrometer.

$^{119}Sn$ Mössbauer spectra were obtained using a YGRS-4M spectrometer. The velocity scale was calibrated relative to $\alpha$-Fe foil. $^{119}Sn$ Mössbauer measurements were carried out at 80K. A $^{119m}SnO_2$ source was used, with a minimum line width of 1.17 mm/s. Sources were kept at room temperature in all cases.

**Table 1** Characterisation of IR and electronic absorption spectra ($\upsilon \times 10^3$ cm$^{-1}$; $\varepsilon$, mol$^{-1}$l cm$^{-1}$) of the macrobicyclic tin-containing cobalt(III) dioximates.

| Compound (Starting dioxime) | $\upsilon$(C=N) | $\upsilon$(N–0) | $\upsilon_1$; $\upsilon_2$; $\upsilon_3$; $\upsilon_4$; $\upsilon_5$ ($\varepsilon_1$); ($\varepsilon_2$); ($\varepsilon_3$; $\varepsilon_4$; $\varepsilon_5 \times 10^4$) |
|---|---|---|---|
| | (cm$^{-1}$) | | |
| (HDEA)[$CoGm_3(SnBr_3)_2$]<br>(glyoxime) | 1564 | 872, 1044,<br>1128, 1176 | 20.9; 25.8; 29.4; 35.9; 40.3<br>(100); (100); (0.28), (1.45), (6.00) |
| (HDEA)[$CoMm_3(SnBr_3)_2$]<br>(methylglyoxime) | 1584 | 924, 1036,<br>1166, 1242 | 20.9; 25.3; 29.5; 36.9; 40.80<br>(100); (100); (0.30), (0.96) , (4.82) |
| (HDEA)[$CoDm_3(SnBr_3)_2$]<br>(dimethylglyoxime) | 1592 | 985, 1092<br>1216 | 21.05; 25.7; 29.9; 37.9; 41.53<br>(100); (100); (0.50), (0.92), (5.42) |
| H[$CoNx_3(SnBr_3)_2$]<br>(cyclohexanedion-1,2-dioxime) | 1590 | 970, 1064,<br>1206 | 20.9; 25.2; 29.5; 37.6; 40.68<br>(100); (100); (0.50), (0.92), (5.42) |
| (HDEA)[$CoNx_3(SnBr_3)_2$] | 1588 | 970, 1064<br>1208 | 20.9; 25.7; 29.5; 37.4; 40.80<br>(100); (100); (0.28) (0.78) (5.36) |
| H[$CoBd_3(SnBr_3)_2$]<br>($\alpha$-benzyldioxime) | 1580 | 896, 1070<br>1124, 1266 | 20.8; 24.8; 29.0; 36.5; 40.54<br>(150); (150); (0.27), (1.55), ( 6.65) |
| (HDEA)[$CoBd_3(SnBr_3)_2$] | 1580 | 892, 1074,<br>1124, 1268 | 21.2; 25.7; 0.37; 1.49; 6.46<br>(150); (150); (0.37), (1.49), (6.46) |
| $FeNx_3(BF)_2$[a] | 1584 | 965, 1070,<br>1225, 1250 | 22.5<br>(1.84) |
| $(HDEA)_2$[$FeNx_3(SnCl_3)_2$][b] | 1568 | 968, 1046 | 17.9; 20.9; 33.56<br>(0.62), (0.72), (1.73) |
| [$CoNx_3(BF)_2$]$(BF)_4$[c] | 1632 | 1035, 1245 | 29.6; 33.50<br>(500); (1.01) |

[a] Reference 1. [b] Reference 2. [c] Reference 9.

### *(HDEA)[CoDm$_3$(SnBr$_3$)$_2$]*

A mixture of dimethylglyoxime (2.32 g, 20 mmol), anhydrous $CoBr_2$ (1.45 g, 6.6 mmol) and $NaOCH_3$ (1.10 g, 20 mmol) in 40 cm$^3$ of isopropanol was heated for 20 min with air bubbling. A solution of 5.84 g of $SnBr_4$ (13.3 mmol) in 20 cm$^3$ of isopropanol was added dropwise with stirring to the yellowish-brown reaction mixture. The mixture was refluxed for 10 min and cooled to room temperature. A solution of DEA in isopropanol (1:2) was added dropwise with stirring to the filtrate obtained, after the separation of the first precipitate, until the solution had an acid reaction. The separated precipitate was washed with diethyl ether, hexane and dried *in vacuo*; yield: 6.14 g, 78%. Analysis for $CoC_{16}H_{30}N_7O_6Sn_2Br_6$: found (calc.): C, 16.24 (16.11); H, 2.55 (2.52); N, 8.14 (8.22)%.

### *H[CoNx$_3$(SnBr$_3$)$_2$]·i-PrOH*

This complex was synthesized by a similar procedure except that nioxime (2.84 g; 20 mmol) was used instead of dimethylglyoxime, without DEA; yield: 3.5 g, 42%. Analysis for $CoC_{21}H_{33}N_6O_7Sn_2Br_6$: found (calc.): C, 20.04 (20.03); H, 2.64 (2.62); N, 6.75 (6.68)%.

### *(HDEA)[CoNx$_3$ (SnBr$_3$)$_2$]*

This complex was obtained as for (HDEA)[$CoDm_3$ $(SnBr_3)_2$]; yield 3.77 g, 45%. Analysis for $CoC_{22}H_{36}N_7O_6Sn_2Br_6$: found (calc.): C, 20.66 (20.79); H, 2.79 (2.83); N, 7.67 (7.72)%.

### *(HDEA)[CoGm$_3$(SnBr$_3$)$_2$]*

This complex was obtained as for (HDEA)[$CoDm_3(SnBr_3)_2$] except that glyoxime (1.76 g, 20 mmol) was used instead of dimethylglyoxime. The complex was recrystallized from acetone-chloroform (1:1); yield: 3.2 g, 44%. Analysis for $CoC_{10}H_{18}N_7O_6Sn_2Br_6$: found (calc.): C, 10.80 (10.82); H, 1.70 (1.62); N, 8.89 (8.84)%.

### *(HDEA)[CoMm$_3$(SnBr$_3$)$_2$]·(CH$_3$)$_2$CO*

This complex was synthesized as for the previous one. Methylglyoxime (2.04 g, 20 mmol) was used instead of glyoxime; yield: 3.9 g, 49%. Analysis for $CoC_{16}H_{30}N_7O_7Sn_2Br_6$: found (calc.): C, 15.97 (15.87); H, 2.52 (2.48); N, 8.10 (8.11)%.

### *H[CoBd$_3$(SnBr$_3$)$_2$]*

This complex was obtained as for H[$CoNx_3(SnBr_3)_2$], except that double the volume of isopropanol and $\alpha$-benzyldioxime (2.40 g, 10 mmol) was used instead of dimethylglyoxime; yield; 2.1 g, 43%. Analysis for $CoC_{42}H_{31}N_6O_6Sn_2Br_6$: found (calc.): C, 33.89 (33.78); H, 2.08 (2.08); N, 5.68 (5.63)%.

### *(HDEA)[CoBd$_3$(SnBr$_3$)$_2$]*

This complex was obtained as with (HDEA)[CoDm$_3$(SnBr$_3$)$_2$], yield: 2.1 g, 41%. Analysis for $CoC_{46}H_{42}N_7O_6Sn_2Br_6$: found (calc.): C, 35.27 (35.24); H, 2.62 (2.68); N, 6.28 (6.26)%.

## RESULTS AND DISCUSSION

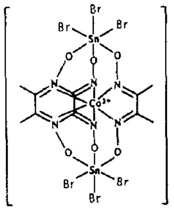
### *Synthesis of complexes*

The range of tin containing macrobicyclic cobalt tris-dioximates turned out to be much narrower than was the case with boron-containing analogues. Attempts to use tin(IV) tetraalkylates or trialkyl halides as cross-linking agents and attempts to cross-link with tin tetrafluoride in the case of cobalt(III) failed. The latter result may be due to difficulties in breaking tin-fluoride bonds and to the formation of side-products such as cobalt(III) and tin(IV) bis-dioximates. It is obvious that steric effects do not play any important part in this case owing to the small size of the fluorine atom.

In the case of $SnBr_4$, the loss of a halide ion appears to be easier than with $SnF_4$, but the large size of the bromine atom leads to unfavourable steric effects owing to its interaction with substituents in the α-dioxime fragments. Thus, attempts to obtain tin bromide clathrochelates of cobalt(III) with α-furyldioxime failed, whereas corresponding tin chloride complexes were identified.[3]

In all cases, a direct template reaction on cobalt(III) ion was used for the synthesis:

$$Co^{2+} + 3H_2D + 2SnBr_4 + 1/4O_2 \xrightarrow[ROH,\ t^0]{NaOCH_3\ (DEA)}$$



$H^+$ (HDEA$^+$)

In the case of some dioximes, it was possible to obtain the complex acids H[CoD$_3$(SnBr$_3$)$_2$], which were isolated without adding amine or by adding a small amount of it. Subsequent addition of equimolar amounts of amines (*e.g.*, diethylamine) results in the formation of corresponding ionic associates. The use of sodium methylate, which is a stronger base than NaOH and is more soluble in isopropanol, leads to the formation of intermediate cobalt(III) tris-dioximates. This is essential for increasing product yield.

### *Structure and Spectra*

IR spectra of the synthesized compounds H(HDEA)[CoD$_3$(SnBr$_3$)$_2$] very much resemble those of similar tin chloride compounds. This applies primarily to the position of N—O and C=N stretches, and the results of previous analysis[3] agree with the data obtained in the present study (Table 1). As expected, $\nu_{C=N}$ frequencies (1580–1588 cm$^{-1}$, with the exception of the glyoxime complex for which the frequencies are much lower: *ca* 1562 cm$^{-1}$) are intermediate between values for corresponding boron-containing cobalt(III) tris-dioximates and tin-containing iron(II) complexes.

The most significant difference in the spectra of the complexes as compared with those of tin chloride compounds is the absence of intense tin-halogen bands. Sn-Br frequencies in octahedral complexes have a much lower value[3] than those corresponding to Sn-Cl and were, therefore, not found in the range examined.

Parameters of electronic absorption spectra of acetonitrile solutions of $H(HDEA)[CoD_3(SnBr_3)_2]$ complexes are very close to those obtained for compounds with the cross-linking $SnCl_3$ group. The most intense ($\varepsilon$ - $(4.5–6.5) \times 10^4$ $mol^{-1}$ $l$ $cm^{-1}$) intramolecular $\pi$ - $\pi^*$ transitions in the range 40000–42000 $cm^{-1}$ mask two Md-L$\pi^*$ charge transfer bands, which were found in the second-order derivative of the spectrum (the first band with an intensity of $(0.8–1.5) \times 10^4$ $mol^{-1}$ $l$ $cm^{-1}$ in the range 36000–38000 $cm^{-1}$ and the second with an intensity of $(3–5) \times 10^3$ $mol^{-1}$ $l$ $cm^{-1}$ in the range 28500–29500 $cm^{-1}$). These bands in turn mask the low-intensity d-d transitions; we did, however, distinguish them using the second-order derivative of the spectrum (Table 1). Ligand field parameters were calculated using equations[13] for cobalt(III) compounds with pseudo-octahedral coordination.

$$\nu_1 = E(^1A_{1g} - {}^1T_{1g}) = 10Dq - C$$

$$\nu_2 = E(^1A_{1g} - {}^1T_{2g}) = 10Dq - C + 16B$$

In such cases it is usually assumed that $C = 4B$, and the ligand field parameters can be calculated as follows:

$$Dq = (3\nu_1 + \nu_2)/40$$

$$B = (\nu_2 - \nu_1)/16$$

Ligand field values obtained are much lower than those calculated for tin chloride and boron-containing tris-dioximate complexes.[3,9]

Chemical shifts in the $^{59}Co$ NMR spectra of cobalt(III) complexes is directly connected with the ligand field force value. The paramagnetic component, $B_0$, which makes the main contribution to the chemical shift value in the NMR spectra of nuclei after helium, may be represented as $B_0 = - 32\beta^2/\Delta r^{-3}$. It is obvious that a decrease in $\Delta$ in the case of tin bromide complexes must lead to an increase in $\delta(^{59}Co)$, and this was observed experimentally. In comparison with $H(HDEA)[CoD_3(SnCl_3)_2]$ compounds, the $^{59}Co$ signals proved to be shifted towards weaker fields by about 2700 ppm.

At the same time, signals in the $^{119}Sn$ spectra were shifted by ~350 ppm towards stronger fields, thus indicating an increase in the ligand field about the tin atom on passing from chloride ($SnO_3Cl_3$) to bromide ($SnO_3Br_3$) coordination. Replacement of a chlorine atom by a bromine usually results in a shift of ~120 ppm.[14] It is evident that replacement of three chlorine atoms by three bromines must causes a 360 ppm shift, in a good agreement with the observed value.

The $^{119}Sn$ NMR chemical shift, which is also determined mainly by paramagnetic contributions, does not, however, reflect the s-electron density on the $^{119}Sn$ nucleus. According to $^{119}Sn$ Mössbauer data, the electron density is much higher for $H(HDEA)$ $[CoD_3(SnBr_3)_2]$ compounds than for their tin chloride analogues, leading to a significant increase in isomeric shifts in the spectra (Table 2). Such an increase

**Table 2** $^1H$, $^{13}C\{^1H\}$, $^{119}Sn$, $^{59}Co$ NMR and $^{119}Sn$ Mössbauer data for the clathrochelate cobalt(III) complexes.

| Compound | $^1H$ relative to TMS (ppm) |  | $^{13}C$ relative to TMS (ppm) |  |  | $^{119}Sn$ relative to $Sn(CH_3)_4$ |  | $^{59}Co$ relative to $K_3[Co(CN)_6]$ |  | $^{119}Sn$ (Mössbauer) |
|---|---|---|---|---|---|---|---|---|---|---|
|  | ($^{H}\backslash C{=}NO$) | (R) | ($^{H}\backslash C{=}NO$) | ($^{R}\backslash C{=}N{=}O$) | (R) | δ, ppm | $\upsilon_{1/2}$, Hz | δ, ppm | $\upsilon_{1/2}$, Hz | δ, mm/s |
| (HDEA)[CoGm$_3$(SnBr$_3$)$_2$] | 7.83 |  | 148.63 |  |  | - 969 | 400 | 7209 | 950 | 0.62 |
| (HDEA)[CoMm$_3$(SnBr$_3$)$_2$]<br>·(CH$_3$)$_2$CO | 7.87,<br>8.02 | 2.51,<br>2.53,<br>2.71 | 151.08,<br>151.27,<br>151.83,<br>152.04 | 159.91,<br>160.09,<br>160.95,<br>161.10 | 13.78,<br>13.91,<br>13.29 | - 996,<br>- 984,<br>- 975,<br>- 965 |  | 7243,<br>7299 | 1530,<br>1190 | 0.68 |
| (HDEA)[CoDm$_3$(SnBr$_3$)$_2$] |  | 2.42 |  | 161.68 | 13.79 | - 995 | 350 | 7313 | 550 |  |
| H[CoNx$_3$(SnBr$_3$)$_2$]·iPrOH |  | 1.77m,<br>3.09m |  | 161.33 | 20.22,<br>26.71 | - 1011 | 500 | 7365 | 1380 | 0.62 |
| (HDEA)[CoNx$_3$(SnBr$_3$)$_2$] |  | 1.74m,<br>3.13m |  | 161.33 | 20.23,<br>26.72 | - 998 | 250 | 7361 | 1400 |  |
| H[CoBd$_3$(SnBr$_3$)$_2$] |  | 7.32,<br>7.34,<br>7.46 |  | 161.12 | 121.61m,<br>128.98,<br>129.48,<br>129.83 | - 1013 | 500 | 7232 | 610 |  |
| (HDEA)[CoBd$_3$(SnBr$_3$)$_2$] |  | 7.32,<br>7.58m |  | 161.23 | 127.27,<br>127.44,<br>128.45,<br>129.49,<br>129.66,<br>130.12 | - 1013 | 500 |  |  | 0.65 |
| (HDEA)[CoNx$_3$(SnCl$_3$)$_2$]$^a$ |  | 1.52m,<br>2.47m |  | 156.14 | 21.31<br>26.09 | - 637.3 |  | 4658 |  | 0.43 |
| (HDEA)$_2$[FeMm$_3$(SnCl$_3$)$_2$]$^b$ | 7.24m | 2 .25m | 146.59m | 154.84m | 12.98 | - 632.4,<br>- 629.9 |  |  |  | 0.42 |

[a] Reference 3. [b] Reference 2.

of charge at the tin atom in the cross-linking group leads to a decrease of ligand field.

$^{59}$Co and $^{119}$Sn NMR spectra make it possible to identify both (*mer* and *fac*) isomers formed by the cross-linking of nonsymmetrical cobalt(III) tris-methylglyoximates by tin(IV) tetrahalides.[3] Similarly to the (HDEA)[CoMm$_3$(SnCl$_3$)$_2$] complex, the $^{59}$Co NMR spectrum of (HDEA) [CoMm$_3$(SnBr$_3$)$_2$] exhibits two lines, and the $^{119}$Sn NMR spectrum exhibits four lines of integrated intensity close to the statistical value (1:3 for *fac* and *mer* isomers, respectively).

Each signal from the azomethine carbon atoms of both types (substituted and unsubstituted) in $^{13}$C NMR spectra consists of four lines, three of which relate to the *mer* isomer, and the fourth to the *fac* isomer, which has $C_3$ symmetry. The presence of isomers is also manifested in $^1$H NMR spectra (Table 2). The $^1$H and $^{13}$C{$^1$H} NMR spectra of other complexes are similar to those of H(HDEA) [CoD$_3$(SnCl$_3$)$_2$] complexes.

Appreciable differences in electron density distributions among the macrobicyclic tin chloride and tin bromide anions seem to be primarily due to steric hindrance. This hindrance gives rise to compounds with a geometry that is not optimal in terms of electronic configuration (primarily low-spin d$^6$ configuration of the cobalt(III) ion). Decrease in electron-donor characteristics in passing from chlorine-containing to bromine-containing cross-linking fragments should be also taken into account. As a result, there is a substantial decrease in the ligand field about the central cobalt(III) ion.

All this is in good agreement with the results of an X-ray structure analysis performed for a readily crystallizing salt of the [CoNx$_3$ (SnBr$_3$)$_2$]$^{2-}$ anion with the

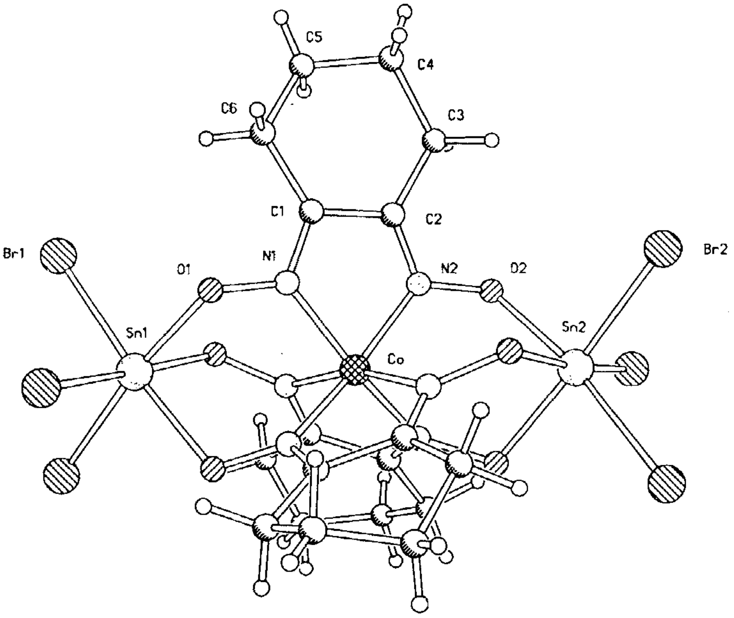


**Figure 1** Perspective view of the [CoNx$_3$(SnBr$_3$)$_2$]$^-$ anion with the labelling scheme used.

bulky tetrabutyl cation $N(n - C_4H_9)^+_4$.[15] In the macrobicyclic anion (Fig. 1), the Co-N distances (1.89Å) are much smaller than those usually observed for cobalt compounds of this type.[3,16] Such a decrease in Co—N bond length leads to a decrease in the distance (2.20Å) between the bases of the coordination polyhedron — a distorted trigonal prism (Fig. 2) — in comparison with the anionic iron(II) complex $FeNx_3(SnCl_3)_2^{2-}$, in which this distance is 2.23Å. The bite angle $\alpha$ (half of the angle in the chelate fragment N—Co—N′) and the distortion angle $\varphi$ (characterizing the degree of deviation of the coordination polyhedron from the trigonal prism) changes in this case only slightly (40.7, 39.5° ($\alpha$) and 39.9, 37.5° ($\varphi$), respectively). It will be noted that slight differences in the metal-nitrogen distance would lead to an increase in basal plane spacing. Any decrease is attributed to the smaller ionic cobalt(III) radius as against iron(II). The distortion angle $\varphi$ in the anion $[CoNx_3(SnBr_3)_2]^-$ is smaller than in its tin chloride analogue $[CoDm_3(SnCl_3)_2]^{2-}$ (42.3°), a fact which may also be due to steric effects leading to a decrease in the ligand field.

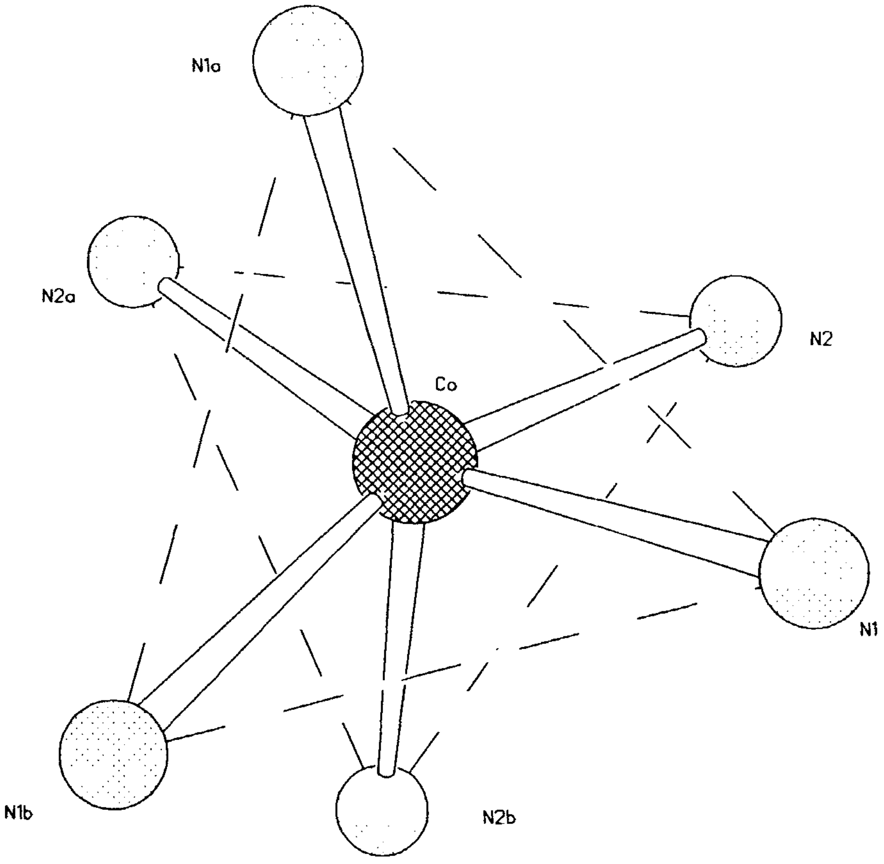


Figure 2 The geometry of the cobalt(III) coordination polyhedron in the $[CoNx_3(SnBr_3)_2]^-$ anion.

## *References*

1. Y.Z. Voloshin, N.A. Kostromina and A.Y. Nazarenko, *Inorg. Chim. Acta*, **170**, 181 (1990), and references therein.
2. Y.Z. Voloshin, N.A. Kostromina, A.Y. Nazarenko and E.V. Polshin, *Inorg. Chim. Acta*, **185**, 83 (1991).
3. Y.Z. Voloshin, V.K. Belsky and V.V. Trachevskii, *Polyhedron*, **11**, 1939 (1992).
4. Y.Z. Voloshin and E.V. Polshin, *Polyhedron*, **11**, 457 (1992).
5. D.R. Boston and N.J. Rose, *J. Am. Chem. Soc.*, **90**, 6859 (1968).
6. S.C. Jackels, J. Zektzer and N.J. Rose. *Inorg. Synth.*, **17**, 139 (1978).
7. D.R. Boston and N.J. Rose, *J. Am. Chem. Soc.*, **95**, 4163 (1973).
8. D. Borchardt and S. Wherland, *Inorg. Chem.*, **25**, 901 (1986).
9. Y.Z. Voloshin, N.A. Kostromina and A.Y. Nazarenko, *Theor. Exp. Khim.*, **26**, 205 (1990).
10. M.A. Murguia, D. Borchardt and S. Wherland, *Inorg. Chem.*, **29**, 1982 (1990).
11. J.G. Muller, K.J. Takeuchi and J.J. Grzybowski, *Polyhedron*, **8**, 1931 (1989).
12. M. Wittenberg and V. Meyer, *Chem. Ber.*, **16**, 500 (1883); L. Claisen, *Chem. Ber.*, **20**, 252 (1887).
13. A.B.P. Lever, *Inorganic Electronic Spectroscopy,*, (Elsevier, Amsterdam, 1984).
14. T.T. Burke and P.C. Lauterbur, *J. Amer. Chem. Soc.*, **83**, 326 (1961).
15. V.E. Zavodnik, personal communication.
16. G.A. Zakrewski, C.A. Chilardi and E.C. Lingafelter, *J. Am. Chem. Soc.*, **93**, 4411 (1971).