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Cobalt(II) and Nickel(II) Complexes with Nitrogen–Sulfur Tripod Ligands. Crystal and Molecular Structure of the Five-coordinate Complex Bromotris(2-tert-butylthioethyl)aminecobalt(II) Hexafluorophosphate (NS_3Br Donor Set)

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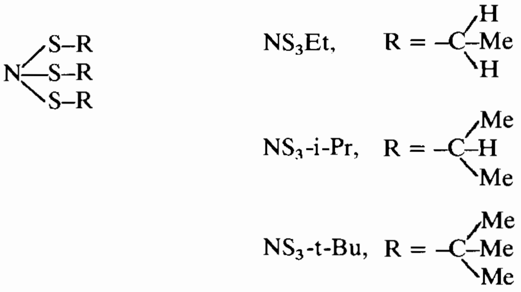
The tripod ligands tris(2-alkylthioethyl)amine, with alkyl = ethyl, iso-propyl, and tert-butyl, give with cobalt(II) and nickel(II) halides high-spin complexes with formulae $[MLX_2]$, $[MLX]Y$, *and* $[MLX]_2[MX_4]$ *(where* $X = Cl, Br, I$; $Y = BPh_4, PF_6$*). The nickel complexes are either six- or five-coordinate: the coordination number decreases as the bulkiness of the alkyl group bound to the sulfur is increased. All the cobalt complexes contain the five-coordinate cation* $[CoLX]^+$. *The crystal and molecular structure of the* $[Co(NS_3\text{-}t\text{-}Bu)Br]PF_6$ *complex has been determined by standard X-ray methods, and refined to* $R = 0.061$. *The crystals are monoclinic, space group* $P2_1/n$. *The unit cell dimensions are:* $a = 27.420\ (2)$, $b = 11.923\ (4)$, $c = 17.082\ (1)$ Å, $\beta = 102.40\ (1)°$, $Z = 8$. *The complex cation has a trigonal bipyramidal geometry with the nitrogen and bromine atoms at the apexes, and the three sulfur atoms in the equatorial plane. The tetrahedral distortion is relatively small (mean Br–Co–S angle = 98.5°), and similar to that found for the* $[Co(Me_6tren)Br]Br$ *complex (*Me_6tren *= tris(2-dimethylaminoethyl)amine).*

Introduction

It is well known that the bulkiness of terminal donor groups in tripod-like ligands has a marked influence on the stereochemistry of the complexes which these ligands form with a number of metal ions.[1] For example, in the series of $NiLX_2$ complexes formed by the tetramine tripod ligands tris(2-R-aminoethyl)amine (tren, R = H; Me_6tren, R = Me; Et_6tren, R = Et) it has been found that the coordination number decreases from six to five as the bulkiness of peripheral donor groups is increased.[1–3]

The symmetric tripod ligand tris(2-methylthioethyl) amine (TSN), with terminal thioether donors, was found to give only five-coordinate cations $[MLX]^+$ with cobalt(II) and copper(II), whereas with nickel(II) only six-coordinate octahedral complexes $[NiLX_2]$ were isolated.[4] It appeared of interest to investigate the effect of increasing the bulkiness of the alkyl groups bound to sulfur on the ability of the ligand to form five-coordinate nickel(II) complexes. We report here the synthesis and characterization of nickel(II) and cobalt(II) complexes formed by the following ligands:



NS_3Et, R = $-CH_2Me$

NS_3-i-Pr, R = $-CH(Me)_2$

NS_3-t-Bu, R = $-C(Me)_3$

The X-ray structure of the complex $[Co(NS_3\text{-}t\text{-}Bu)Br]PF_6$ with NS_3Br donor set has also been undertaken, as part of a systematic research on structural features of trigonal bipyramidal cobalt(II) complexes.[1,5,6]

Experimental

The synthesis of the ligands has been reported.[7]

Preparation of the Complexes. Tetraphenylborate Complexes

To a hot solution of the requisite metal salt (2 mmol) in butan-1-ol (10 ml) was added the ligand (2.4 mmol) in butan-1-ol (10 ml) followed by $NaBPh_4$ (2 mmol) in the same solvent (15 ml). Usually the complexes crystallized immediately. They were filtered, washed with butan-1-ol and petroleum ether, recrystallized from acetone–ethanol, and dried *in vacuo* at 60°C. Yield, 70–80%.

The $[Co(NS_3\text{-}t\text{-}Bu)Br]PF_6$ complex was similarly obtained by addition of $[Bu_4N]PF_6$ to the metal salt–ligand solution in ethanol.

$[MLX_2]$ and $[MLX]_2[MX_4]$ Complexes

To a hot solution of the metal salt (2 mmol) in butan-1-ol (15 ml) was added the ligand (2 mmol) in the same solvent (5 ml). The solution was filtered, concentrated, treated with a small amount of cyclohexane, and stored in a desiccator until crystallization was complete (usually overnight). The complexes were recrystallized with the same procedure from butan-1-ol—cyclohexane, filtered, washed with butan-1-ol and petroleum ether, and dried as above. Yield, about 70%.

Materials and Physical Measurements

All solvents were reagent grade. All physical measurements were carried out as described previously.[4,8,9]

Results and Discussion

The analytical and magnetic data for the complexes are reported in Table I. All the complexes are of the high-spin type. The magnetic moments range from 3.11–3.58 BM for the nickel complexes, and from 4.45–4.63 BM for the cobalt complexes.

Nickel Complexes

Complexes with formulae $[NiLX]BPh_4$ (X = Cl, Br, I), $[NiLX_2]$ and $[NiLX]_2[NiX_4]$ were isolated (Table I). Their electronic spectra in the solid state and in solution all display either of two types of pattern, *i.e.* those characteristic of an octahedral structure ($^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ at 8.5–9.8 kK; $\rightarrow {}^3T_{1g}(F)$ at 13.7–16.1 kK; $\rightarrow {}^3T_{1g}(P)$ at 22.7–25 kK) and of a five-coordinate trigonal bipyramidal structure (in C_{3v} symmetry: $^3E(F) \rightarrow {}^3E(F)$ at 6.1–6.9 kK; $\rightarrow ({}^3A_1, {}^3A_2(F))$ at 10.5–11.2 kK; $\rightarrow {}^3A_2(F)$ at 14.7–16 kK; $\rightarrow {}^3E(P)$ at 20–22 kK; $\rightarrow {}^3A_2(P)$ at 24–25 kK)[1,10,11] respectively (Table II; Figure 1). For $[NiLX]_2[NiX_4]$ complexes the spectral features are the sum of those for a five-coordinate cation and a tetrahedral anion $[NiX_4]^{2-}$. The stereochemistries assigned to the complexes on the basis of spectrophotometric, conductometric and molecular weight measurements are summarized in Table III. It appears that if no specific counter-ion is added, neutral six-coordinate $[NiLX_2]$ complexes are obtained, however the sterically most hindered NS_3-t-Bu ligand forms $[NiLX]_2[NiX_4]$ auto-complexes. Counter-anions of low coordinating power precipitate ionic [NiLX]Y complexes, where the cation is five-coordinate except with ligands (L = NS_3–Et; X = Cl) whose less-exacting steric requirements allow six-coordination to be attained *via* polymerization in the solid state.

Cobalt Complexes

All three ligands react with cobalt(II) bromide to form only five-coordinate $[CoLBr]^+$ complexes. This behavior, different from that of nickel, agrees with the

TABLE I. Analytical and Magnetic Data for the Complexes.

Compound	Color	M.p.[a]	Found (%)				Reqd (%)				μ_{eff} (BM)[b]
			C	H	N	Metal	C	H	N	Metal	
$[Ni(NS_3\text{-}Et)Cl]BPh_4$	Green	203–205	62.3	6.9	1.9	8.6	62.30	6.82	2.02	8.47	3.28(26)
$[Ni(NS_3\text{-}Et)Br]BPh_4$	Green	194–196	58.2	6.3	1.8	7.8	58.48	6.41	1.89	7.95	3.31(26)
$[Ni(NS_3\text{-}Et)I]BPh_4$	Brown	188–190	54.4	6.1	1.8	7.4	55.10	6.02	1.78	7.47	3.18(26)
$[Ni(NS_3\text{-}i\text{-}Pr)Cl]BPh_4$	Green	175–177	63.9	7.3	2.0	8.0	63.50	7.25	1.90	7.95	3.25(26.5)
$[Ni(NS_3\text{-}i\text{-}Pr)Br]BPh_4$	Olive green	175–177	59.5	7.0	1.7	7.6	59.95	6.84	1.78	7.52	3.25(26)
$[Ni(NS_3\text{-}i\text{-}Pr)I]BPh_4$	Brown–green	198–202	56.9	6.7	1.6	7.1	56.50	6.44	1.69	7.08	3.24(26)
$[Ni(NS_3\text{-}t\text{-}Bu)Cl]BPh_4$	Mustard	190d	64.1	7.9	1.7	7.7	64.70	7.64	1.80	7.53	3.51(26.5)
$[Ni(NS_3\text{-}t\text{-}Bu)Br]BPh_4$	Red–brown	184d	61.4	7.4	1.6	7.0	61.30	7.23	1.70	7.13	3.58(26.5)
$[Ni(NS_3\text{-}t\text{-}Bu)I]BPh_4$	Brown	166d	57.2	7.0	1.6	6.5	58.00	6.84	1.61	6.75	3.42(26.5)
$[Ni(NS_3\text{-}Et)Cl_2]$	Green	148–150	34.9	6.9	3.4	14.4	35.10	6.62	3.41	14.30	3.19(26)
$[Ni(NS_3\text{-}Et)Br_2]$	Green	174–177	28.5	5.6	2.9	11.5	28.80	5.44	2.80	11.73	3.16(26)
$[Ni(NS_3\text{-}Et)I_2]$	Mustard	203–205	24.2	4.8	2.4	9.9	24.26	4.58	2.35	9.90	3.11(26)
$[Ni(NS_3\text{-}i\text{-}Pr)Cl_2]$	Green	160–162	40.3	7.7	3.2	12.9	39.80	7.33	3.09	12.95	3.23(26)
$[Ni(NS_3\text{-}i\text{-}Pr)Br_2]$	Green	160–162	33.4	6.4	2.7	10.7	33.20	6.13	2.58	10.83	3.22(26)
$[Ni(NS_3\text{-}i\text{-}Pr)I_2]$	Brown–green	140–142	28.6	5.6	2.3	9.0	28.30	5.22	2.20	9.23	3.14(26)
$[Ni(NS_3\text{-}t\text{-}Bu)Br]_2[NiBr_4]$	Brown–green	162–165	30.6	5.6	2.0	12.4	31.20	5.67	2.02	12.70	3.44(26.5)
$[Ni(NS_3\text{-}t\text{-}Bu)I]_2[NiI_4]$	Red–brown	142–145	25.7	4.8	1.7	10.7	25.87	4.71	1.67	10.53	3.33(26.5)
$[Co(NS_3\text{-}Et)Br]BPh_4$	Violet	196d	58.8	6.7	1.8	7.7	58.50	6.40	1.89	7.96	4.45(26.5)
$[Co(NS_3\text{-}i\text{-}Pr)Br]BPh_4$	Magenta	190d	60.3	7.1	1.6	7.9	59.95	6.84	1.78	7.54	4.46(25)
$[Co(NS_3\text{-}t\text{-}Bu)Br]PF_6$	Purple–violet	200d	33.7	6.3	2.1	8.8	33.35	6.05	2.16	9.08	4.50(26.5)
$[Co(NS_3\text{-}Et)Br]_2[CoBr_4]$	Red–violet	173d	23.4	4.7	2.3	14.5	23.65	4.46	2.30	14.50	4.52(26.5)
$[Co(NS_3\text{-}i\text{-}Pr)Br]_2[CoBr_4]$	Purple	173–176	27.9	5.3	2.3	13.3	27.64	5.10	2.15	13.55	4.63(26)
$[Co(NS_3\text{-}t\text{-}Bu)Br]_2[CoBr_4]$	Purple–violet	176d	31.1	5.6	1.9	12.5	31.15	5.67	2.02	12.72	4.54(26.5)

[a] d = decomposition. [b] Temp. (° C) in parentheses.

TABLE II. Electronic Spectral Data for the Complexes.

Compound	State[a]	Absorption Max (kK) with $\varepsilon_{\mathrm{molar}}$ for Soln. in Parentheses
$[\mathrm{Ni(NS_3{-}Et)Cl]BPh_4}$	R	9.5, 15.6, 25.0sh
	N	6.9(28), 9.5(36), 10.9(36), 16.1(53), 23.8(150)
$[\mathrm{Ni(NS_3{-}Et)Br]BPh_4}$	R	9.6, 14.2, 23.5sh
	N	6.9(39), 9.2(29), 11.0(37), 16.0(70)
$[\mathrm{Ni(NS_3{-}Et)I]BPh_4}$	R	9.85, 16.1
	D	6.7(61), 11.2(48), 15.6(117), 22.2sh, 28.2(3393)
$[\mathrm{Ni(NS_3{-}i{-}Pr)Cl]BPh_4}$	R	9.3, 13.9, 25.0sh
	N	6.7(22), 9.3(35), 10.9(35), 14.7(45), 20.0sh, 23.5(145)
$[\mathrm{Ni(NS_3{-}i{-}Pr)Br]BPh_4}$	R	6.7, 9.1, 11.1, 15.6, 22.2sh
	D	6.5(46), 9.1(29), 11.0(41), 15.5(80), 22.2sh
$[\mathrm{Ni(NS_3{-}i{-}Pr)I]BPh_4}$	R	6.7, 11.3, 16.0, 22.2sh, 26.7
	N	6.9(50), 11.0(48), 15.5(95), 20.0sh
$[\mathrm{Ni(NS_3{-}t{-}Bu)Cl]BPh_4}$	R	6.7, 10.75, 14.7, 18.2sh, 22.0sh, 25.0
	N	6.8(48), 9.75(37), 10.6(49), 15.15(56), 20.0sh, 22.5(255)
$[\mathrm{Ni(NS_3{-}t{-}Bu)Br]BPh_4}$	R	6.8, 11.1, 14.7, 20.0sh, 25.0
	N	6.7(52), 9.5(31), 10.9(46), 14.9(67), 20.0sh, 22.2sh
$[\mathrm{Ni(NS_3{-}t{-}Bu)I]BPh_4}$	R	6.15, 10.5, 14.3, 18.2sh, 21.3, 26.3
	N	6.45(78), 9.1(39), 10.75(62), 16.0(111), 21.1(620)
$[\mathrm{Ni(NS_3{-}Et)Cl_2]}$	R	9.1, 14.7, 23.8
	N	8.9(40), 10.7sh, 15.5(28), 23.8(59)
$[\mathrm{Ni(NS_3{-}Et)Br_2]}$	R	9.1, 14.7, 23.8
	N	9.0(38), 14.1(34), 23.5(73)
$[\mathrm{Ni(NS_3{-}Et)I_2]}$	R	9.3, 15.1, 25.0sh
	N	9.4(43), 15.15(65)
$[\mathrm{Ni(NS_3{-}i{-}Pr)Cl_2]}$	R	8.6, 14.2, 23.3
	N	8.6(37), 10.75(12), 13.4sh, 14.3(24), 15.15sh, 17.5sh, 23.0(53)
$[\mathrm{Ni(NS_3{-}i{-}Pr)Br_2]}$	R	8.5, 13.7, 22.7
	N	8.6(42), 10.25sh, 13.9(33), 16.7sh, 22.5(84)
$[\mathrm{Ni(NS_3{-}I{-}Pr)I_2]}$	R	8.7, 14.0, 23.5sh
	D	8.5(46), 13.7(64), 23.5sh
$[\mathrm{Ni(NS_3{-}t{-}Bu)Br]_2[NiBr_4]}$	R	6.8, 11.1, 14.8, 19.4sh, 25.0, 27.4
	N	7.2(125), 8.5(135), 11.2(140), 13.3sh, 14.3sh, 15.9(310)
$[\mathrm{Ni(NS_3{-}t{-}Bu)I]_2[NiI_4]}$	R	6.8, 11.0, 13.8, 18.5, 20.0, 25.9
	N	6.6(180), 11.5(310), 12.5sh, 14.8(460)
$[\mathrm{Co(NS_3{-}Et)Br]BPh_4}$	R	5.9, 11.1sh, 14.3, 20.0
	D	5.7(49), 12.1sh, 14.3(188), 20.4(533)
$[\mathrm{Co(NS_3{-}i{-}Pr)Br]BPh_4}$	R	5.7, 12.1sh, 13.9, 19.4
	D	5.6(53), 12.05(67), 14.3(181), 18.7(311)
$[\mathrm{Co(NS_3{-}t{-}Bu)Br]PF_6}$	R	5.15, 12.1sh, 13.9, 18.9
	N	5.2(95), 11.8(95), 13.7(175), 14.2sh, 18.5(360)
$[\mathrm{Co(NS_3{-}Et)Br]_2[CoBr_4]}$	R	5.3, 11.9sh, 14.1, 19.4
	N	5.2(116), 11.9sh, 14.5(1050), 16.4(620), 19.4(365)
$[\mathrm{Co(NS_3{-}i{-}Pr)Br]_2[CoBr_4]}$	R	5.4, 11.75sh, 14.0, 19.05
	D	5.5(174), 12.0(109), 13.7(1114), 14.2(1083), 14.9(621), 15.5(310), 16.1sh, 18.9(514)
$[\mathrm{Co(NS_3{-}t{-}Bu)Br]_2[CoBr_4]}$	R	*ca.* 5.1, 12.1, 14.5, 18.9, 23.2sh
	N	< 5.0, 7.4(60), 11.8(51), 14.5(604), 15.0sh, 16.3(470), 18.5(270)

[a] R = diffuse reflectance; N = nitroethane soln; D = 1,2-dichloroethane soln.

well known preference of cobalt(II) for five-coordination rather than six-coordination.[1,3,9,12] If no counter-ion is added, auto-complexes $[\mathrm{CoLBr]_2[CoBr_4]}$ are formed in every case, as frequently found.[4,9]

The electronic spectra of $[\mathrm{CoLBr}]^+$ complex cations (Figure 1) correlate with those previously found for high-spin trigonal bipyramidal cobalt(II) complexes.[1,3,4,9] The spectral assignment (in C_{3v} symmetry: ${}^4A_2(F) \rightarrow {}^4E(F)$ at 5.0–5.9 kK; $\rightarrow {}^4E(F)$ at 11.1–12.5 kK; $\rightarrow {}^4A_2(P)$ at 13.9–14.3 kK; $\rightarrow {}^4E(P)$ at 18.9–20 kK) has been substantiated by single-crystal polarized spectral studies.[13]

TABLE III. Stereochemistries Assigned to the Nickel Complexes.[a]

Compound	L	NS$_3$Et		NS$_3$-i-Pr		NS$_3$-t-Bu	
	X	Solid	Soln	Solid	Soln	Solid	Soln
[NiLX]BPh$_4$	Cl	6	5^b	6	5^b	5	5
	Br	6	5	5	5	5	5
	I	6	5	5	5	5	5
[NiLX$_2$] or [NiLX]$_2$[NiX$_4$]	Cl	6	6	6	6		
	Br	6	6	6	6	5+4	5+4
	I	6	6^c	6	6^c	5+4	5+4

[a] 6 = six-coordinate octahedral; 5 = five-coordinate; 4 = tetrahedral anion. [b] Partially associated. [c] Partially dissociated.

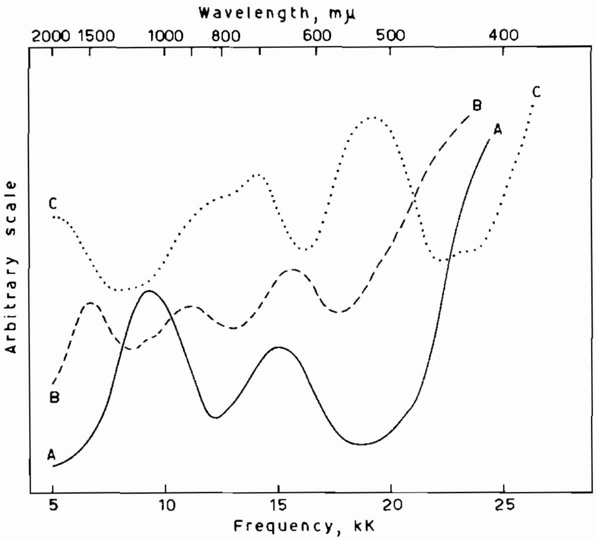


Figure 1. Reflectance spectra of: A, [Ni(NS$_3$-i-Pr)Cl]BPh$_4$; B, [Ni(NS$_3$-i-Pr)Br]BPh$_4$; C, [Co(NS$_3$-t-Bu)Br]PF$_6$.

X-Ray Structure of [Co(NS$_3$-t-Bu)Br]PF$_6$

Crystal data

$C_{18}H_{39}F_6NCoS_3PBr$, m = 649.57, monoclinic, a = 27.420 (2), b = 11.923 (4), c = 17.082 (1) Å, β = 102.40 (1)°, U = 5454.3 Å^3, D_m = 1.58 (by flotation), Z = 8, D_c = 1.591. Space group $P2_1/n$ from systematic absences: h0l with h+l = 2n+1 and 0k0 with k = 2n+1 (there are two independent molecules in the asymmetric unity). Zr-filtered Mo-K_α radiation, λ = 0.70926 Å, μ(Mo-K_α) = 25.47 cm^{-1}.

Data collection

The crystal used for the collection (grown from acetone–ethanol) had dimensions 0.2 × 0.5 × 0.13 mm, coincident with [100], [010], and [001] directions. Intensity data were collected with a Hilger & Watts four-circle automatic diffractometer by the ω–2ϑ scan technique. Scans of 70 s, with steps of 0.01° and a count of 1 s for each step, were taken across the peaks; background was counted for 35 s on each side of the peak. Three reflections were monitored as standards every 50 measurements. 2685 reflections having $I \geqq 3\sigma$ (I) were measured in the range $0 < 2\vartheta < 40°$. The intensities and their standard deviations were calculated according to ref. 14. The observed intensities were corrected for Lorentz and polarization effects. An absorption correction was applied by numerical methods, using Hamilton's GONO9 programme with local modifications; transmission coefficients ranged from 0.63 to 0.75. Scattering factors for non-hydrogen atoms were taken from ref. 15, and from ref. 16 for hydrogen atoms. Anomalous dispersion effects for cobalt and bromine atoms were included in the calculation of F_c.[17]

*Structure determination and refinement**

The structure was solved by direct methods, obtaining signs for the normalized structure factors by the symbolic addition procedure for centrosymmetric crystals.[18] These calculations were performed using F.S. Ahmed's programme SAP. The signs of 466 reflections, having $E \geqq 1.5$, were determined and used in the E-map calculation. This map revealed the positions of the cobalt, bromine, sulfur and phosphorus atoms of the two independent molecules. Two successive Fourier syntheses showed all non-hydrogen atoms. At this point R factor was 0.26. These calculations were made with an IBM 1130 computer, using a series of programmes for the A.R.C., Unit of Structural Chemistry, University College (London). Refinement was then undertaken by means of full-matrix least-squares cycles.[19] The minimized function was $\Sigma w(|F_o|-|F_c|)^2$, in which w is the weight assigned according to the Hughes scheme: w = 1 for reflections with $F_o \leqq 50$, $\sqrt{w} = 50/F_o$ for reflections with $F_o > 50$.

Individual isotropic temperature factors were used for carbon atoms, whereas all the heavier atoms were

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* Observed and calculated structure factors are available from the authors on request.

TABLE IV. Positional Parameters ($\times 10^4$) and Isotropic Temperature Factors, with Estimated Standard Deviations in Parentheses.

Atom	x/a	y/b	z/c	B(Å^2)
Br	4594(1)	2263(2)	–108(1)	*
Co	4009(1)	2371(1)	751(1)	*
S(1)	3806(1)	434(3)	778(2)	*
S(2)	4529(1)	3222(3)	1895(2)	*
S(3)	3405(1)	3528(3)	–50(2)	*
P	2072(2)	1856(4)	3008(3)	*
F(1)	1743(5)	2910(11)	2917(8)	*
F(2)	2387(5)	779(11)	3100(10)	*
F(3)	2549(5)	2544(13)	2989(9)	*
F(4)	2199(5)	1953(16)	3929(7)	*
F(5)	1982(6)	1773(13)	2074(7)	*
F(6)	1614(4)	1140(11)	3032(12)	*
N	3445(4)	2455(9)	1579(7)	*
C(1)	3355(6)	1324(14)	1869(10)	5.2(0.4)
C(2)	3276(6)	479(14)	1208(11)	5.5(0.4)
C(3)	3627(6)	3177(14)	2291(11)	5.5(0.4)
C(4)	4171(6)	2977(15)	2681(10)	5.4(0.4)
C(5)	2949(6)	2940(14)	1130(10)	5.0(0.4)
C(6)	3035(6)	3933(15)	635(10)	5.4(0.4)
C(7)	3584(5)	–230(13)	–198(9)	4.5(0.3)
C(8)	3269(7)	570(15)	–821(11)	6.2(0.4)
C(9)	3276(7)	–1265(18)	–76(13)	7.7(0.5)
C(10)	4032(6)	–589(15)	–486(11)	6.2(0.4)
C(11)	5140(5)	2567(11)	2300(8)	3.7(0.3)
C(12)	5111(7)	1313(17)	2224(12)	7.1(0.5)
C(13)	5335(6)	2945(16)	3179(11)	6.4(0.4)
C(14)	5478(6)	3069(15)	1737(11)	5.7(0.4)
C(15)	3628(6)	4816(14)	–411(10)	4.9(0.4)
C(16)	3757(7)	4502(16)	–1224(11)	6.7(0.5)
C(17)	3172(7)	5633(16)	–608(11)	6.5(0.4)
C(18)	4042(7)	5352(17)	202(12)	6.8(0.5)
Br′	4717(1)	2831(2)	–5037(1)	*
Co′	4097(1)	2539(1)	–4261(1)	*
S(1)′	3826(1)	4426(3)	–4201(2)	*
S(2)′	4620(1)	1777(3)	–3081(2)	*
S(3)′	3600(1)	1250(3)	–5169(2)	*
P′	2023(2)	3017(4)	–2028(3)	*
F(1)′	1734(5)	1930(10)	–1990(9)	*
F(2)′	2285(6)	4152(13)	–2070(12)	*
F(3)′	2522(5)	2459(15)	–1912(11)	*
F(4)′	2124(6)	3241(17)	–1104(9)	*
F(5)′	1923(7)	2894(14)	–2961(8)	*
F(6)′	1526(5)	3664(14)	–2165(14)	*
N′	3512(4)	2234(10)	–3556(7)	*
C(1)′	3367(6)	3262(16)	–3192(11)	6.2(0.4)
C(2)′	3298(5)	4277(13)	–3727(10)	4.5(0.3)
C(3)′	3662(8)	1451(18)	–2929(14)	7.9(0.5)
C(4)′	4184(6)	1579(14)	–2449(11)	5.3(0.4)
C(5)′	3053(8)	1841(19)	–4085(14)	8.8(0.6)
C(6)′	3129(6)	867(14)	–4642(10)	5.1(0.4)
C(7)′	3557(5)	5116(11)	–5177(8)	3.3(0.3)
C(8)′	3222(7)	4331(16)	–5761(12)	6.7(0.5)
C(9)′	3284(7)	6130(16)	–5019(11)	6.1(0.4)
C(10)′	3999(8)	5499(18)	–5485(13)	7.6(0.5)
C(11)′	5122(5)	2665(13)	–2501(9)	4.4(0.3)
C(12)′	4915(9)	3756(22)	–2300(16)	9.2(0.7)

* These atoms were refined anisotropically.

TABLE IV. (Cont.)

Atom	x/a	y/b	z/c	B(Å^2)
C(13)′	5384(6)	2095(16)	−1765(11)	6.5(0.4)
C(14)′	5490(9)	2869(21)	−3041(15)	9.4(0.6)
C(15)′	3873(5)	−75(13)	−5330(9)	4.3(0.3)
C(16)′	4263(8)	124(18)	−5891(13)	7.6(0.5)
C(17)′	3460(9)	−851(21)	−5775(15)	9.2(0.6)
C(18)′	4167(7)	−656(17)	−4575(12)	7.2(0.5)

TABLE V. Anisotropic Thermal Parameters with Estimated Standard Deviations in Parentheses.[a]

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Br	5.4(0.1)	7.5(0.1)	4.3(0.1)	0.5(0.1)	2.2(0.1)	−0.5(0.1)
Co	3.6(0.1)	2.9(0.1)	2.9(0.1)	0.2(0.1)	0.7(0.1)	−0.2(0.1)
S(1)	4.8(0.2)	2.7(0.2)	3.7(0.2)	0.3(0.2)	0.7(0.2)	−0.2(0.2)
S(2)	3.9(0.2)	3.6(0.2)	3.1(0.2)	0.1(0.1)	0.2(0.1)	−0.2(0.2)
S(3)	4.5(0.2)	2.7(0.2)	3.9(0.2)	0.5(0.1)	0.2(0.2)	0.1(0.2)
P	4.8(0.2)	4.5(0.2)	4.5(0.3)	−0.1(0.2)	0.7(0.2)	0.0(0.2)
F(1)	11.3(0.8)	7.7(0.7)	11.5(1.0)	2.1(0.6)	2.7(0.7)	−0.3(0.7)
F(2)	8.4(0.8)	8.3(0.8)	18.7(1.4)	4.0(0.6)	1.8(0.8)	0.1(0.8)
F(3)	11.1(0.9)	13.9(1.1)	11.6(1.0)	−5.5(0.8)	3.8(0.7)	−1.0(0.8)
F(4)	11.6(0.9)	21.4(1.5)	5.2(0.7)	4.0(1.0)	1.6(0.6)	0.8(0.8)
F(5)	21.2(1.4)	13.1(1.1)	4.0(0.6)	−3.0(1.0)	0.6(0.7)	−1.9(0.6)
F(6)	6.3(0.7)	8.6(0.8)	27.1(1.9)	−1.1(0.6)	2.4(0.9)	7.5(1.0)
N	4.7(0.6)	2.9(0.6)	3.2(0.6)	1.0(0.4)	1.0(0.5)	−0.1(0.5)
Br′	5.1(0.1)	6.5(0.1)	4.2(0.1)	−0.4(0.1)	1.7(0.1)	0.1(0.1)
Co′	3.6(0.1)	3.0(0.1)	2.8(0.1)	−0.2(0.1)	0.3(0.1)	−0.1(0.1)
S(1)′	4.2(0.2)	3.0(0.2)	3.2(0.2)	−0.2(0.1)	0.0(0.1)	0.0(0.2)
S(2)′	4.2(0.2)	3.3(0.2)	3.1(0.2)	0.1(0.1)	0.2(0.1)	−0.1(0.2)
S(3)′	4.7(0.2)	2.8(0.2)	4.1(0.2)	−0.2(0.2)	−0.5(0.2)	0.0(0.2)
P′	4.9(0.2)	4.6(0.2)	4.5(0.3)	−0.1(0.2)	0.4(0.2)	−0.5(0.2)
F(1)′	13.8(1.0)	6.4(0.7)	14.4(1.2)	−3.4(0.7)	2.3(0.8)	1.0(0.7)
F(2)′	13.4(1.1)	9.6(1.0)	18.9(1.6)	−5.5(0.9)	−0.7(1.0)	0.9(1.0)
F(3)′	9.8(0.9)	17.2(1.4)	14.6(1.3)	6.6(0.9)	−0.4(0.8)	−1.7(1.0)
F(4)′	15.4(1.2)	22.8(1.8)	6.8(0.9)	−6.0(1.2)	3.3(0.8)	−4.0(1.0)
F(5)′	19.3(1.4)	14.0(1.1)	5.5(0.7)	0.4(1.0)	1.5(0.8)	0.4(0.7)
F(6)′	8.6(0.9)	11.1(1.1)	27.5(2.1)	2.1(0.8)	−0.2(1.0)	−8.7(1.3)
N′	4.6(0.6)	2.7(0.6)	3.8(0.6)	−0.6(0.5)	0.0(0.5)	0.3(0.5)

[a] The temperature factor is defined as: $\exp(-1/4 \sum_i \sum_j B_{ij}h_ih_ja_i^*a_j^*)$.

refined anisotropically. A difference Fourier synthesis calculated at R = 0.074 showed the positions of 61 hydrogen atoms, which were introduced in the subsequent calculations in fixed positions, with a temperature factor B = 6.0 Å^2. Two more cycles gave a final R of 0.061 (R_w = 0.090). Corresponding atoms in the two independent molecules of the asymmetric unity are roughly correlated by a glide plane *c* at y = 1/4.

Final values of the atomic parameters with their estimated standard deviations are reported in Tables IV–VI. Standard deviations were calculated according to the expression: $\sigma_j = [\Sigma w(\Delta F)^2 a^{jj}/(m-n)]^{1/2}$, where m is the number of reflections, n is the number of parameters refined and a^{jj} is the jjth element of the inverse least-squares matrix.

Description of the structure

The coordination polyhedron of the $[Co(NS_3\text{-t-Bu})Br]^+$ cation consists of a fairly regular trigonal bipyramid, with the nitrogen and bromine atoms at the apexes and the three sulfur atoms in the equatorial plane (Figure 2). Bond lengths and angles in the coordination polyhedron and in the ligand molecule are reported in Tables VII–VIII. The values of the Co–N distance (2.23 and 2.31 Å in the two independent molecules), of the Br–Co–S mean angle (98.5°) and of the displacement of the metal from the basal plane towards the apical bromine atom (0.35 Å) are all very close to those found for the $[Co(Me_6tren)Br]^+$ complex cation (2.15 Å, 99°, and 0.32 Å respectively).[20] These parameters are indicative of a relatively small tetrahedral

TABLE VI. Positional Parameters ($\times 10^3$) of Hydrogen Atoms (numbered according to the atom to which they are attached).

Atom	x/a	y/b	z/c
H(1,1)	304	128	194
H(1,2)	366	150	207
H(2,1)	306	–28	133
H(2,2)	296	70	84
H(3,1)	334	314	256
H(3,2)	362	376	196
H(4,2)	427	228	281
H(5,2)	285	230	72
H(6,1)	321	448	94
H(6,2)	266	434	32
H(8,1)	305	11	–129
H(8,2)	297	65	–68
H(8,3)	354	76	–93
H(9,1)	320	–136	–62
H(9,2)	304	–98	10
H(9,3)	359	–136	–11
H(10,1)	390	–104	–110
H(10,2)	425	–93	1
H(10,3)	419	6	–70
H(12,2)	492	126	260
H(13,1)	572	294	327
H(13,2)	510	278	355
H(13,3)	541	350	295
H(14,1)	553	274	216
H(14,2)	557	420	181
H(14,3)	534	290	112
H(16,2)	415	450	–106
H(17,1)	348	588	–55
H(17,2)	300	580	–30
H(17,3)	320	556	–119
H(18,2)	384	572	68
H(18,3)	434	490	31
H(1′,1)	375	364	–258
H(1′,2)	296	324	–299
H(2′,2)	296	415	–428
H(3′,2)	369	70	–338
H(4′,1)	422	240	–219
H(4′,2)	437	188	–178
H(5′,1)	296	160	–370
H(5′,2)	291	234	–439
H(6′,2)	279	62	–510
H(8′,1)	307	472	–635
H(8′,2)	290	434	–564
H(8′,3)	350	412	–584
H(9′,1)	304	624	–550
H(9′,2)	304	590	–486
H(9′,3)	350	676	–459
H(10′,1)	403	596	–587
H(10′,2)	415	592	–507
H(10′,3)	425	494	–555
H(12′,1)	522	430	–181
H(12′,2)	475	364	–197
H(13′,2)	500	210	–151
H(14′,1)	531	358	–290
H(14′,2)	560	214	–296
H(16′,3)	394	40	–610
H(17′,1)	370	–130	–562
H(17′,2)	320	–100	–549
H(17′,3)	315	–50	–612
H(18′,2)	388	–66	–435
H(18′,3)	436	–24	–412

TABLE VII. Bond Lengths (Å) and Angles (°), with Estimated Standard Deviations, in the Coordination Polyhedron.

	Molecule 1	Molecule 2
Co–Br	2.398(3)	2.395(3)
Co–S(1)	2.378(4)	2.378(4)
Co–S(2)	2.384(4)	2.388(4)
Co–S(3)	2.354(4)	2.391(4)
Co–N	2.311(11)	2.232(11)
Br–Co–N	179.4(0.4)	178.7(0.3)
Br–Co–S(1)	98.6(0.1)	98.7(0.1)
Br–Co–S(2)	99.4(0.1)	98.8(0.1)
Br–Co–S(3)	98.9(0.1)	96.2(0.1)
S(1)–Co–N	80.8(0.3)	82.1(0.3)
S(2)–Co–N	80.8(0.3)	81.6(0.3)
S(3)–Co–N	81.4(0.3)	82.5(0.3)
S(1)–Co–S(2)	119.9(0.1)	117.4(0.1)
S(1)–Co–S(3)	116.2(0.1)	119.7(0.1)
S(2)–Co–S(3)	116.7(0.1)	117.3(0.1)

TABLE VIII. Average Values of the Distances (Å) in the Ligand Molecule and in Hexafluorophosphate, with their Average Standard Deviations.

	Molecule 1	Range	Molecule 2	Range
S–C	1.81(2)	1.76–1.85	1.81(2)	1.78–1.86
N–C	1.49(2)	1.47–1.52	1.45(2)	1.41–1.47
C–C	1.53(2)	1.48–1.59	1.52(2)	1.47–1.60
P–F	1.54(1)	1.53–1.56	1.54(1)	1.50–1.56

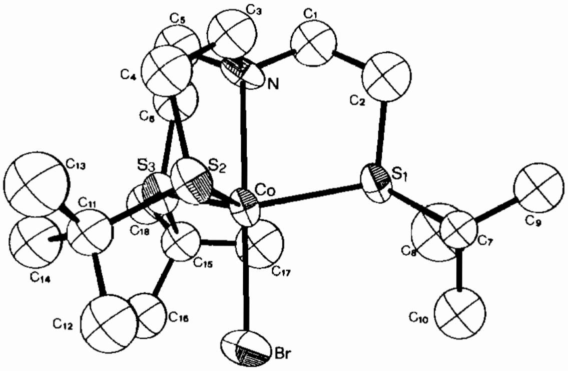

Figure 2. A perspective view of the complex cation $[Co(NS_3\text{-}t\text{-}Bu)Br]^+$.

distortion. The absence of a strong coordinative distortion similar to that found in trigonal bipyramidal cobalt(II) complexes with phosphorus in the donor set[1,5] allows the $\Sigma\chi$ and $\Sigma n°$ criterions to be applied.[1,5,21] This application correctly predicts the high-spin state of these complexes,[5] confirming the already noted low spin-pairing capacity of thioethereal sulfur in chelating nitrogen–sulfur ligands.[4,9]

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