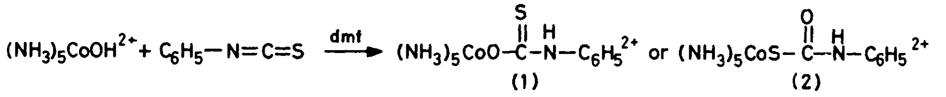
Reactions of Co-ordinated Nucleophiles. Preparation, Characterization, and Crystal Structure of Penta-ammine(phenylthiocarbamato-*S*)cobalt(III) Perchlorate Monohydrate

By **Robert J. Balahura,* George Ferguson,* Lynda Ecott,** and **Pik Yuen Siew,** Guelph-Waterloo Centre for Graduate Work in Chemistry, Department of Chemistry, University of Guelph, Guelph, Ontario, Canada N1G 2W1

The title complex $[Co(NH_3)_5(SCONHPh)][ClO_4]_2$ has been prepared by the addition of $[Co(NH_3)_5(OH_2)][ClO_4]_3$ to phenyl isothiocyanate in dimethylformamide. A mechanism for formation of the complex is proposed whereby an *O*-bonded complex is initially formed and then isomerizes rapidly to the stable *S*-bonded species. The stable complex has been characterized by spectroscopic methods and by *X*-ray crystallography. Crystals are orthorhombic, space group *Pnam*, with eight molecules of the hydrate, $[Co(NH_3)_5(SCONHC_6H_5)][ClO_4]_2 \cdot H_2O$, in a unit cell of dimensions $a = 9.573(5)$, $b = 11.300(5)$, and $c = 37.40(2)$ Å. The structure was refined by full-matrix least-squares calculations to a final *R* value of 0.096 for 860 ' observed ' reflections. The Co atom is octahedrally co-ordinated [Co–N 1.98—2.02(3), Co–S 2.264(9) Å]. An extensive network of hydrogen bonds links the cations, anions, and water molecules.

REACTIONS involving co-ordinated hydroxide have been established for a variety of metal complexes. Thus, $[Co(NH_3)_5(OH)]^{2+}$ reacts rapidly [1] with propionic anhydride at pH 8.0 to yield the propionato-complex, $[Co(NH_3)_5(OCOC_2H_5)]^{2+}$; it was also shown that the reaction proceeds with retention of the cobalt–oxygen bond. However, in subsequent studies [2,3] it was determined that the degree of retention is dependent on the solvent used. For triethyl phosphate as solvent the reaction of $[Co(NH_3)_5(^{18}OH)]^{2+}$ with acetic anhydride yields $[Co(NH_3)_5(^{18}OCOCH_3)]^{2+}$ as the only product. For more polar solvents such as dimethylformamide (dmf) the originally formed acetato-complex labelled in the metal-bound oxygen positions undergoes isomerization, giving finally a mixture of acetato-complex labelled in both the metal-bound oxygen position and the uncomplexed carbonyl oxygen position.

We have utilized the nucleophilic character of co-ordinated hydroxide in dmf to add to phenyl isothiocyanate as shown below. We had initially expected to obtain complex (1) but, due to the earlier findings [2,3] and the nucleophilicity of sulphur, anticipated obtaining compound (2) as well. In this paper we report that the product of the reaction of $[Co(NH_3)_5(OH)]^{2+}$ with phenyl isothiocyanate in dimethylformamide is exclusively (2) and describe its preparation, characterization, and crystal structure.



$$(NH_3)_5CoOH^{2+} + C_6H_5{-}N{=}C{=}S \xrightarrow{dmf} (NH_3)_5CoO{-}\overset{\overset{S}{\|}}{C}{-}\overset{H}{N}{-}C_6H_5^{\,2+} \text{ or } (NH_3)_5CoS{-}\overset{\overset{O}{\|}}{C}{-}\overset{H}{N}{-}C_6H_5^{\,2+}$$

(1) (2)

EXPERIMENTAL

*Synthesis of Penta-ammine(phenylthiocarbamato-*S*)-cobalt*(III) *Perchlorate.*—Phenyl isothiocyanate (Eastman, 2.5 cm³, 0.021 mmol) was added to a solution containing penta-ammine(aqua)cobalt(III) perchlorate (5 g, 0.022 mmol) *NN*-dimethylbenzylamine (3 cm³, 0.022 mmol), and dimethylformamide (15 cm³). This solution was stirred for 2 h at room temperature during which time the colour changed from red to reddish brown. The complex was precipitated by the addition of a 50 : 50 mixture (1 000 cm³) of butan-2-ol and diethyl ether. The complex was purified by cation-exchange chromatography on Sephadex C-25-120 resin. Elution was accomplished using increasing concentrations of sodium chloride from 0.025 to 0.10 mol dm⁻³. A red band corresponding to a 2+ ion was removed from the column and isolated as the perchlorate salt (Found: C, 16.7; H, 4.15; N, 16.8. Calc. for $[Co(NH_3)_5(SCONHC_6H_5)][ClO_4]_2$: C, 17.0; H, 4.25; N, 17.0%).

Crystals for *X*-ray analysis were grown from a dilute solution of perchloric acid. The crystals obtained were small plates which did not diffract well and proved on *X*-ray analysis to be those of a monohydrate.

Crystal Data.—$C_7H_{23}Cl_2CoN_6O_{10}S$, $M = 513.2$, Orthorhombic, $a = 9.573(5)$, $b = 11.300(5)$, $c = 37.40(2)$ Å, $U = 4\,045.7$ Å³, $Z = 8$, $F(000) = 2\,112$, $D_c = 1.685$ g cm⁻³, $\lambda(\text{Mo-}K_\alpha) = 0.710\,69$ Å, $\mu(\text{Mo-}K_\alpha) = 11.9$ cm⁻¹, space group *Pnam* or $Pna2_1$ (from systematic absences $0kl$ when $k + l = 2n + 1$, $h0l$ when $h = 2n + 1$); *Pnam* assumed and confirmed by structure analysis.

Preliminary investigation of the crystals was by Weissenberg and precession photography. The lattice parameters were obtained from a least-squares analysis of the setting angles of reflections with $\theta(\text{Mo-}K_\alpha)$ in the range 10—15° measured on a Hilger and Watts Y290 diffractometer.

Intensity data were collected using graphite-monochromatized radiation and processed in the usual way.[4] One octant of reciprocal space was surveyed with $1 < \theta < 20°$. A total of 1 921 independent reflections was measured of which the 860 with $I > 3\sigma(I)$ were labelled ' observed ' and used in the determination and refinement of the structure; the data were then corrected for Lorentz, polarization, and absorption effects.

Determination of the Structure.—The position of the cobalt atom was found from a three-dimensional Patterson function and the remaining non-hydrogen atoms were obtained from a subsequent heavy-atom-phased Fourier summation.

TABLE 1

Final fractional co-ordinates (× 10^4) for $[Co(NH_3)_5(SCONHC_6H_5)][ClO_4]_2{\cdot}H_2O$ with estimated standard deviations in parentheses

Atom	*X/a*	*Y/b*	*Z/c*
Co	1 706(3)	204(3)	1 494(1)
S	2 767(8)	1 616(8)	1 161(3)
Cl(1)	2 265(8)	6 127(9)	1 207(3)
Cl(2)	3 857(14)	3 814(15)	2 500 *
Cl(3)	4 157(16)	8 688(17)	2 500 *
N(1)	2 394(23)	2 717(19)	562(6)
N(2)	899(26)	−1 085(23)	1 808(7)
N(3)	1 123(24)	−636(20)	1 053(6)
N(4)	2 294(25)	1 097(23)	1 926(7)
N(5)	−48(22)	1 150(19)	1 504(7)
N(6)	3 491(24)	−683(19)	1 502(8)
C(1)	1 777(31)	1 989(23)	781(7)
C(2)	1 882(33)	3 220(26)	246(8)
C(3)	2 381(33)	4 217(28)	123(8)
C(4)	1 900(41)	4 840(35)	−195(10)
C(5)	942(36)	4 254(30)	−390(10)
C(6)	387(38)	3 234(34)	−275(10)
C(7)	863(40)	2 566(41)	36(10)
O(1)	488(21)	1 638(18)	743(5)
O(2)	610(27)	3 621(24)	1 816(7)
O(11)	1 008(29)	6 789(25)	1 175(8)
O(12)	3 053(47)	6 607(38)	1 482(13)
O(121)	3 105(71)	6 940(54)	1 010(16)
O(13)	2 770(65)	6 078(62)	819(17)
O(131)	2 553(52)	5 076(50)	1 004(15)
O(14)	1 993(52)	4 926(48)	1 252(52)
O(141)	2 405(80)	5 618(74)	1 536(24)
O(21)	3 277(40)	4 123(32)	2 178(10)
O(22)	5 056(76)	4 470(63)	2 500 *
O(23)	4 055(12)	2 688(102)	2 500 *
O(31)	4 386(45)	8 104(38)	2 195(11)
O(32)	2 817(50)	9 063(41)	2 500 *
O(33)	4 704(88)	9 802(87)	2 500 *

* Fixed value.

TABLE 2

Interatomic distances (Å) and angles (°) in $[Co(NH_3)_5(SCONHC_6H_5)][ClO_4]_2{\cdot}H_2O$ with estimated standard deviations in parentheses

(*a*) Bond lengths

Co–S	2.264(9)	C(6)–C(7)	1.46(5)
Co–N(2)	2.02(3)	Cl(1)–O(11)	1.42(3)
Co–N(3)	1.98(2)	Cl(1)–O(12)	1.39(5)
Co–N(4)	1.99(3)	Cl(1)–O(121)	1.43(6)
Co–N(5)	1.99(2)	Cl(1)–O(13)	1.53(7)
Co–N(6)	1.98(2)	Cl(1)–O(131)	1.44(5)
S–C(1)	1.76(3)	Cl(1)–O(14)	1.39(5)
C(1)–O(1)	1.30(3)	Cl(1)–O(141)	1.37(9)
C(1)–N(1)	1.30(3)	Cl(2)–O(21)	1.37(4)
N(1)–C(2)	1.40(3)	Cl(2)–O(22)	1.37(7)
C(2)–C(3)	1.31(4)	Cl(2)–O(23)	1.29(11)
C(2)–C(7)	1.46(5)	Cl(3)–O(31)	1.34(4)
C(3)–C(4)	1.46(4)	Cl(3)–O(32)	1.35(5)
C(4)–C(5)	1.35(5)	Cl(3)–O(33)	1.36(9)
C(5)–C(6)	1.34(4)		

(*b*) Cation bond angles

S–Co–N(2)	175.7(8)	N(5)–Co–N(6)	177(1)
S–Co–N(3)	90.4(7)	Co–S–C(1)	112(1)
S–Co–N(4)	87.8(8)	S–C(1)–O(1)	122(2)
S–Co–N(5)	90.6(7)	S–C(1)–N(1)	115(2)
S–Co–N(6)	88.8(7)	O(1)–C(1)–N(1)	123(3)
N(2)–Co–N(3)	92(1)	C(1)–N(1)–C(2)	129(3)
N(2)–Co–N(4)	90(1)	N(1)–C(2)–C(3)	121(3)
N(2)–Co–N(5)	93(1)	N(1)–C(2)–C(7)	119(3)
N(2)–Co–N(6)	88(1)	C(3)–C(2)–C(7)	119(3)
N(3)–Co–N(4)	178(1)	C(2)–C(3)–C(4)	126(3)
N(3)–Co–N(5)	92(1)	C(3)–C(4)–C(5)	115(4)
N(3)–Co–N(6)	91(1)	C(4)–C(5)–C(6)	121(4)
N(4)–Co–N(5)	87(1)	C(5)–C(6)–C(7)	125(4)
N(4)–Co–N(6)	90(1)	C(6)–C(7)–C(2)	112(4)

It was obvious from this map that one of the perchlorate groups was disordered over two sites and that the asymmetric unit contained two additional half perchlorate groups lying on a mirror plane in *Pnam*. An additional peak was also found in a general position and because of its density and location was attributed to an oxygen atom from a water of solvation. Because of the relatively few data with $I > 3\sigma(I)$, only the Co, Cl, and S atoms were allowed anisotropic motion in the refinement. No allowance was made for hydrogen atoms. Full-matrix least-squares calculations [5] with unit weights converged with $R = 0.096$. A final-difference map showed no maxima of chemical significance although there were a number of small peaks around the disordered perchlorate group.

Atomic scattering factors were taken from ref. 6. The final fractional co-ordinates and standard deviations are in Table 1 and main details of molecular geometry are in Table 2. Tables of thermal parameters, other dimensions, together with observed and calculated structure factors have been deposited as Supplementary Publication No. SUP 23225 (12 pp).* Figure 1 is a view of the ions and water molecule with the atom-numbering scheme and Figure 2 is a stereoview of the packing.

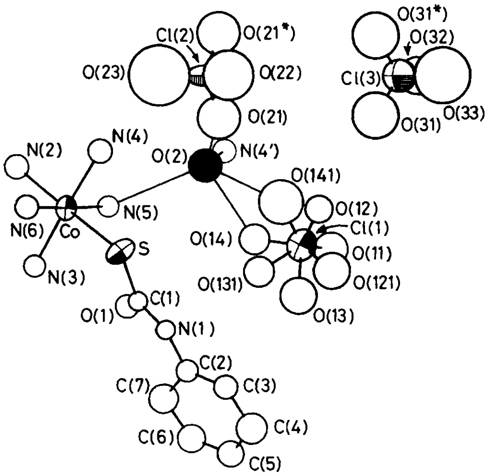


FIGURE 1 A view of the ions and water molecule (filled circle) with the atom-numbering scheme

RESULTS AND DISCUSSION

The synthetic reaction was based on the early work of Jackman *et al.* [2,3] and Buckingham and Engelhardt [1] who had shown that $[Co(NH_3)_5(OH)]^{2+}$ was an effective nucleophile and could be exploited in the preparation of penta-amminecarboxylatocobalt(III) complexes. A reasonable mechanism for the reaction of penta-ammine(hydroxo)cobalt(III) with phenyl isothiocyanate is given below. It was anticipated that (1) would be a major product but under our reaction conditions only (2) was isolated (see below). Also, there is no evidence for a substitution reaction producing $[Co(NH_3)_5(SCNC_6H_5)]^{3+}$.

The carbon, hydrogen, and nitrogen analysis and the chromatography elution characteristics are consistent with either (1) or (2) but the preparative route and known inertness of cobalt(III) favour the production of the *O*-

---

* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

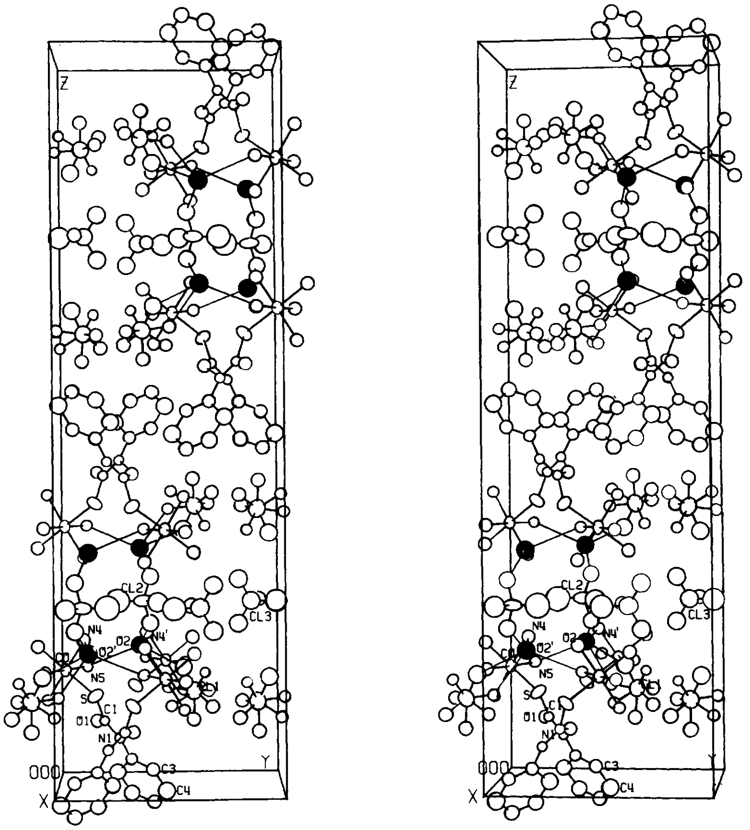


FIGURE 2 A stereoview of the crystal structure, thin lines indicate possible hydrogen bonds. The filled circle represents the water molecule

bonded isomer. However, the u.v.–visible and n.m.r. spectra of the complex provide the first clue that a cobalt–sulphur bond is present. The pertinent characteristics of these spectra are given in Table 3. The most characteristic feature of the electronic absorption spectrum is the intense band at 262 nm. A band in this region of the spectrum has been taken as being diagnostic of cobalt–sulphur bonding[7] and has been assigned as a ligand-to-metal charge-transfer band. This is predicted when sulphur is co-ordinated to a potentially oxidizing centre. Ligand-to-metal charge-transfer bands have been observed for cobalt(III) co-ordinated to thiolato-,[8] thioether,[9] disulphide,[10] sulphinato-,[11] sulphito-,[12] thiocyanato-,[13] and thiosulphato-ligands.[14]

TABLE 3

Electronic absorption and proton magnetic resonance spectral data for penta-ammine(phenylthiocarbamato-*S*)cobalt(III) perchlorate

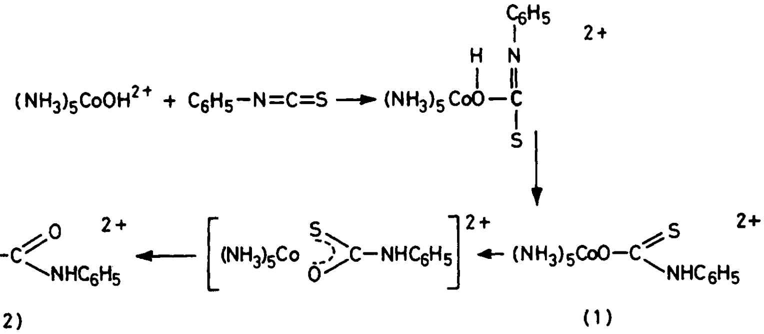
(*a*) Electronic absorption bands/nm[a] 510 (98.6), 302 (sh), 262 (24 200)

(*b*) Proton magnetic resonance[b]

trans-NH_3	3.44
cis-NH_3	3.24
C_6H_5	7.58—6.98
N–H	10.1

[a] Spectrum is identical in both 0.1 mol dm^{-3} $HClO_4$ and water. Values of ϵ (dm^3 mol^{-1} cm^{-1}) are given in parentheses.
[b] In [$^2H_6$]dimethyl sulphoxide. Values in δ with respect to $SiMe_4$.

The ^1H n.m.r. spectrum contains the expected resonances for either structure (1) or (2). However, it has been pointed out previously that the difference between

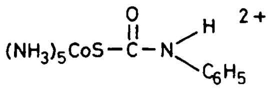


the *cis*- and *trans*-NH_3 chemical shifts is characteristic of the donor atom for penta-amminecobalt(III) complexes.[15] For oxygen donors the chemical-shift difference (*cis* — *trans*) is δ 1—1.5 whereas for sulphur donors this shift is δ −0.5 to 0. The data in Table 3 give a chemical-shift difference of −0.20 thus indicating a cobalt–sulphur bond, which was established unequivocally by our *X*-ray analysis.

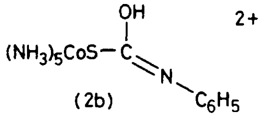
The $[Co(NH_3)_5(SCONHC_6H_5)]^{2+}$ cation (Figure 1) is composed of an octahedrally co-ordinated cobalt atom bonded to five NH_3 ligands with *cis* N–Co–N angles of 87—93(1)° and a thiocarbamato-moiety with N–Co–S angles 87.8—90.6(7)°. The Co–S bond length [2.264(9) Å] is similar to that reported[14] for $[Co(NH_3)_5(S_2O_3)]^+$ [2.287(1) Å] and the Co–S–C angle 112(1)° is close to tetrahedral. The Co–N bond lengths are not sufficiently well determined to allow any discussion of a possible *trans* effect of the sulphur ligand; the Co–N bond *trans* to S [Co–N(2) 2.02(3) Å] is not significantly longer than those *trans* to N [1.98—1.99(3) Å]. The remaining bond lengths in the cation (Table 1) are in accord with accepted values.

In the crystal structure (Figure 2) the distances between the water molecule, the perchlorate ions, and cations are indicative of hydrogen bonding [$O(H_2O) \cdots$ O(perchlorate), 2.89—3.31; $O(H_2O) \cdots NH_3$, 3.09—3.31; O(perchlorate) $\cdots NH_3$, 2.99—3.36; O(carbonyl) $\cdots NH_3$ 2.89, 2.95; and O(carbonyl) $\cdots$ NH 3.12 Å] but as no hydrogen atoms were located with certainty because of the poor quality of the data, no hydrogen-bonding scheme is proposed.

The i.r. spectrum of the complex shows the expected vibrations of co-ordinated NH_3 in the 3 000, 1 600, 1 315, and 830 cm^{-1} regions. Deuteriation of the complex shifts these vibrations to lower frequency and, in the case of the 1 600 cm^{-1} region of the spectrum, exposes two bands at 1 595 and 1 575 cm^{-1}. These can be attributed to C=N and C=O stretches respectively. These data indicate a contribution of both (2a) and (2b) to the structure and the cation dimensions, although not very precise [C–O 1.30, C–N 1.30(3) Å], are consistent with this formulation. There is also an intercation hydrogen bond linking these groups *via* a C=O $\cdots$ HN or C–OH $\cdots$ N linkage (O $\cdots$ N 3.12 Å). Finally, it is worth noting that the 2 000—2 300 cm^{-1} region of the spectrum is devoid of bands expected if the starting ligand, phenyl isothiocyanate, were complexed to cobalt(III).



(2a)



(2b)

Two of us (R. J. B. and G. F.) are grateful to NSERC (Canada) for the award of operating grants.

[1/1360 *Received*, 24*th August*, 1981]

REFERENCES

[1] D. A. Buckingham and L. M. Engelhardt, *J. Am. Chem. Soc.*, 1975, **97**, 5915.

[2] L. M. Jackman, R. M. Scott, R. H. Portman, and J. F. Dormish, *Inorg. Chem.*, 1979, **18**, 1497.

[3] L. M. Jackman, J. F. Dormish, R. M. Scott, R. H. Portman, and R. D. Minard, *Inorg. Chem.*, 1979, **18**, 1503.

[4] P. J. Roberts, G. Ferguson, R. G. Goel, W. Ogini, and R. J. Restivo, *J. Chem. Soc., Dalton Trans.*, 1976, 898.

[5] G. M. Sheldrick, SHELX Crystallographic Computing Program, University Chemical Laboratories, Cambridge, 1976.

[6] 'International Tables for *X*-Ray Crystallography,' The Kynoch Press, Birmingham, 1974, vol. 4.

[7] C. J. Weschler and E. Deutsch, *Inorg. Chem.*, 1973, **12**, 2682 and refs. therein.

[8] C. J. Weschler and E. Deutsch, *Inorg. Chem.*, 1976, **15**, 139.

[9] R. C. Elder, G. J. Kennard, M. Payne, and E. Deutsch, *Inorg. Chem.*, 1978, **17**, 1296.

[10] M. Woods, J. Karbwang, J. C. Sullivan, and E. Deutsch, *Inorg. Chem.*, 1976, **15**, 1678.

[11] B. A. Lange, K. Libson, E. Deutsch, and R. Elder, *Inorg. Chem.*, 1976, **15**, 2985.

[12] R. C. Elder, M. J. Heeg, M. Payne, M. Trkula, and E. Deutsch, *Inorg. Chem.*, 1978, **17**, 481.

[13] C. J. Shea and A. Haim, *Inorg. Chem.*, 1973, **12**, 3013.

[14] R. J. Restivo, G. Ferguson, and R. J. Balahura, *Inorg. Chem.*, 1977, **16**, 167.

[15] R. J. Balahura and R. B. Jordan, *Inorg. Chem.*, 1970, **9**, 1567.