Synthesis and Characterization of Bis(hydrazinium)tetra(thiocyanato-*N*)-cobalt(II) and -nickel(II) Dihydrates; Crystal Structure of the Cobalt Complex†

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Bis(hydrazinium)tetra(thiocyanato-*N*)cobalt-(II) and -nickel(II) dihydrates, $(N_2H_5)_2M(NCS)_4{\cdot}2H_2O$ (M = Co or Ni) have been prepared by the reaction of the corresponding $N_2H_5M(N_2H_3CO_2)_3{\cdot}H_2O$ with thiocyanic acid. The structure of the cobalt complex has been determined by single-crystal X-ray diffraction studies. The cobalt ion is six-co-ordinated with an octahedral geometry generated by two hydrazinium cations and four N-bonded thiocyanate ligands. Of significance is the presence of both linear and angular Co–NCS linkages (in the same molecule) and the $N_2H_5^+$ ions in *cis* positions. The nickel complex is isostructural with the cobalt complex.

Co-ordination compounds containing positively charged ligands are rare in marked contrast with those of neutral and negatively charged ligands and are of interest.[1–3] Among the known cationic polyamine ligands, monoprotonated hydrazine (the hydrazinium cation) is unique as the site of positive charge is immediately adjacent to the N-donor atom.[4–7] A variety of complexes containing $N_2H_5^+$, *e.g.* hydrazinium metal sulphates,[7–11] oxalates,[12–14] hydrazinecarboxylates,[15] chlorides[16–18] and fluorides[19–20] are known. It is not surprising that there are no reports on the hydrazinium metal complexes of thiocyanates as the usual method of preparation, *viz.* from the aqueous solutions of the metal thiocyanates and hydrazinium thiocyanate, always resulted in the formation of metal thiocyanate hydrazines.[21] The preparation of the hydrazinium metal thiocyanate complexes of cobalt and nickel has now been achieved from the reaction of the corresponding hydrazinium metal hydrazinecarboxylates and thiocyanic acid. The products have been characterized by spectral and structural studies.

Experimental

Reagents.—The compounds $N_2H_5M(N_2H_3CO_2)_3{\cdot}H_2O$ (M = Co or Ni) were prepared from the metal salts, hydrazine hydrate and carbon dioxide as reported.[15] Dilute thiocyanic acid (<5%) was prepared from barium thiocyanate[22] and sulphuric acid.

Preparation of Complexes.—$(N_2H_5)_2Co(NCS)_4{\cdot}2H_2O$. Freshly prepared solid $N_2H_5Co(N_2H_3CO_2)_3{\cdot}H_2O$ was added to dilute thiocyanic acid (500 cm^3) in small portions while maintaining the reaction temperature around 0 °C. The solid decomposed with the evolution of carbon dioxide to give a purple solution. The addition of solid was continued till the solution became neutral. The resulting solution was allowed to stand open to the atmosphere at room temperature. Dark purple crystals separated in 6–8 weeks. They were removed from the solution, dried by pressing between filter paper and stored in an air-tight bottle [Found: Co, 14.9; N_2H_4, 16.2; NCS, 59.9. Calc. for $(N_2H_5)_2Co(NCS)_4{\cdot}2H_2O$: Co, 15.0; N_2H_4, 16.8; NCS, 59.0%].

$(N_2H_5)_2Ni(NCS)_4{\cdot}2H_2O$. This complex was prepared in a similar way, but the reaction gave a dark blue crystalline mass which was found to be $Ni(NCS)_2(N_2H_3CSNH_2)_2$.[23] The solution later gave a light blue crystalline solid which was dried with filter paper and stored in an air-tight bottle. [Found: Ni, 15.0; N_2H_4, 16.4; NCS, 59.6. Calc. for $(N_2H_5)_2Ni(NCS)_4{\cdot}2H_2O$: Ni, 14.9; N_2H_4, 16.8; NCS, 59.18%].

Chemical Analysis.—Metal contents were estimated by titrating with ethylenediaminetetraacetate, thiocyanate by Volhard's method.[24] Hydrazine was determined by titrating against 0.025 mol dm^{-3} KIO_3 under Andrews conditions[3,24] after the removal of thiocyanate as silver thiocyanate since thiocyanate interferes in the hydrazine estimation.

Physical Measurements.—Infrared spectra of the samples in the region 4000–600 cm^{-1} were recorded as Nujol mulls using a Perkin-Elmer 781 spectrophotometer, electronic spectra in the visible region using a Hitachi U-3400 spectrophotometer. The spectra in the solid state were obtained by dispersing the samples in Nujol.

X-Ray Crystallography.—The crystals were mounted after sealing in Lindemann capillary tubes. Cell constants and corresponding standard deviations were obtained from a least-squares refinement of 25 reflections automatically centred on a Nonius CAD-4 diffractometer. Based on the cell volume of 1554.2 Å^3 and four formula units in the cell, the calculated density of 1.685 g cm^{-3} is in good agreement with that of 1.68 g cm^{-3}, obtained by flotation using a mixture of chloroform and bromoform.

Data collection and processing. Intensity data were collected on a Nonius CAD-4 diffractometer using graphite monochromated Mo-Kα radiation in ω–2θ mode with a scan width of 0.85 ± 0.35tanθ.

Structure solution and refinement. The structure was solved by conventional Patterson and Fourier techniques and refined by full-matrix least-squares procedures with anisotropic thermal parameters for non-hydrogen atoms. Hydrogen atoms were located in the Fourier difference map and were included without refinement. All the details regarding the data collection and refinement are listed in Table 1.

Major calculations were carried out on a DEC-1090 computer using the SHELX 76 system of programs;[25] ORTEP

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

Table 1 Details of the crystallographic analysis for $(N_2H_5)_2Co(NCS)_4\cdot 2H_2O$

M_r	392.9	Crystal colour	Dark purple
Crystal system	monoclinic	Crystal dimensions (mm)	0.4 × 0.2 × 0.2
λ(Mo-Kα)	0.710 69 Å	2θ range	2–54
T/K	293	reflections measured	$\pm h,k,l$
Space group	$C2/c$	No. measured	2140
a/Å	16.283(4)	No. unique	1927
b/Å	7.717(8)	No. of data used	1684
c/Å	13.318(4)		$[F > 5.0\sigma(F)]$
β/°	111.76(2)	μ(Mo-Kα)/cm^{-1}	16.3
U/Å^3	1554.2	$(\Delta/\sigma)_{max}$	0.001
Z	4	R_{int}	0.069
$F(000)$	804	R	0.049

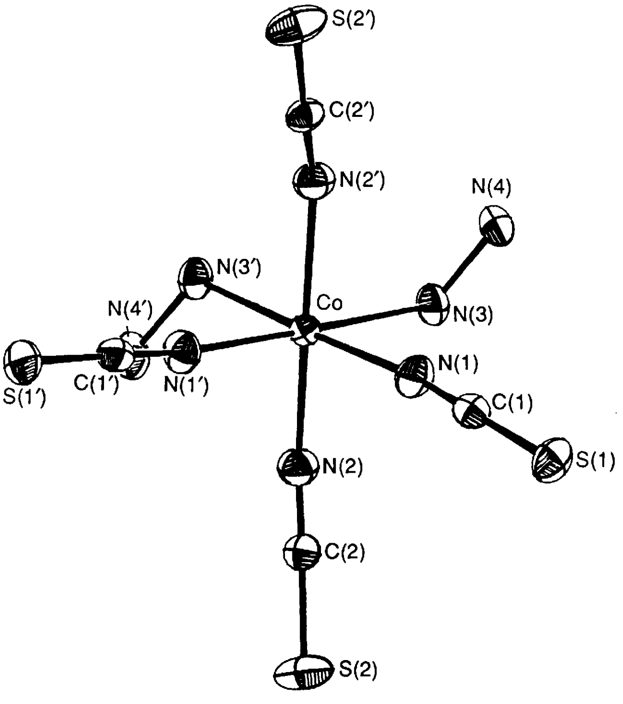


Fig. 1 ORTEP diagram of $[Co(N_2H_5)_2(NCS)_4]$ showing the atom numbering scheme. Ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity

II[26] and PLUTO[27] programs were used for the diagrams. Scattering factor data for cobalt were taken ref. 28 and for the other atoms the values available in SHELX 76 were used.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates and thermal parameters.

Results and Discussion

Since the reaction between metal thiocyanates and hydrazinium thiocyanates could not be used to prepare hydrazinium metal thiocyanate complexes, an alternate method *viz.* decomposing hydrazinium metal hydrazinecarboxylates with dilute thiocyanic acid (< 5%) has been employed. The reaction is exothermic and is accompanied by the decomposition of carboxylate and the evolution of carbon dioxide [equation (1)]

$$N_2H_5M(N_2H_3CO_2)_3\cdot H_2O(s) + 6HSCN(aq) \longrightarrow M^{2+}(aq) + 4N_2H_5^{+}(aq) + 6NCS^{-}(aq) + 3CO_2(g) \quad (1)$$

Slow concentration of the solution at room temperature gave the desired complex in the case of cobalt. However, nickel initially gave a thiosemicarbazide complex and later the hydrazinium complex in small amounts. This anomaly can be attributed to the rearrangement of hydrazinium thiocyanate to thiosemicarbazide[29] and the stability of nickel thiosemicarbazide complexes.[30,31] The complexes $(N_2H_5)_2M(NCS)_4\cdot 2H_2O$ (M = Co or Ni) are very hygroscopic, readily soluble in water and decompose when exposed to air.

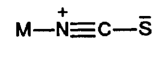
Electronic Spectra.—The solid-state electronic spectral data (in the visible region) for the complexes are as follows along with their assignments: cobalt, 19 500 $[{}^4T_{1g}(F) \longrightarrow {}^4A_{2g}(F)]$ and 20 400 $[{}^4T_{1g}(F) \longrightarrow {}^4T_{1g}(P)]$; nickel, 17 300 $[{}^3A_{2g}(F) \longrightarrow {}^3T_{1g}(F)]$ and 23 000 cm^{-1} $[{}^3A_{2g}(F) \longrightarrow {}^3T_{1g}(P)]$. These data indicate octahedral arrangements around the metal ions.[32,33]

Infrared Spectra.—Infrared spectra of both the complexes show absorption bands in the region 990–1010 cm^{-1} (995 for cobalt and 1000 cm^{-1} for nickel). These bands clearly indicate the presence of co-ordinated $N_2H_5^+$ ions.[34] The spectra also show strong bands (doublets) near 2100 cm^{-1} (2100 and 2130 for cobalt, 2105 and 2135 cm^{-1} for nickel) assigned to N–C stretching of the NCS group. The N–C stretching frequency of thiocyanate, when it is terminal N-bonded, is known[35] to occur in the region 2050–2100 cm^{-1} and there is some overlap with the corresponding region for the terminal S-bonded form [ν(C–N) 2083–2130 cm^{-1}]. Thiocyanate complexes of nickel(II) and cobalt(II) are found to contain the NCS ligand either terminal N- or N,S-bridge bonded.[35] Interestingly, the infrared spectra of both complexes exhibit two sharp peaks (doublets) indicating the presence of two kinds of NCS groups.

Although from these data it is possible to suggest that the metal ions are surrounded by two hydrazinium cations and four terminal N-bonded NCS ions, it is difficult to perceive the presence of two different kinds of thiocyanate groups. Further, it is not possible to predict from these results alone the relative positions of the $N_2H_5^+$ and NCS ligands. For this reason a single-crystal X-ray structural analysis of $(N_2H_5)_2Co(NCS)_4\cdot 2H_2O$ has been carried out.

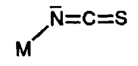
Structure of $(N_2H_5)_2Co(NCS)_4\cdot 2H_2O$.—The crystal contains discrete $(N_2H_5)_2Co(NCS)_4$ and H_2O molecules. The co-ordination around the cobalt atom is essentially octahedral. The cobalt atoms lie on the two-fold axes. The structure with the atom numbering scheme is shown in Fig. 1 (symmetry-related atoms are indicated with primes). Fractional atomic co-ordinates and the interatomic distances and angles are listed in Tables 2 and 3 respectively.

The cobalt atom is six-co-ordinated by two hydrazinium ions and four thiocyanate ions. All the four thiocyanate groups are terminal N-bonded. The most interesting feature of the structure is the presence of two kinds of NCS groups. Two of the four have angular Co–NCS linkages and the other two have linear ones [Fig. 2(*a*) and (*b*)]. The linear Co–NCS groups are *cis* to each other and the bent ones are *trans* to each other. The presence of two kinds of Co–NCS groups can be understood as the M–NCS linkage is known[36] to occur in both linear and bent forms.



$$M{-}\overset{+}{N}{\equiv}C{-}\overset{-}{\underline{S}}$$

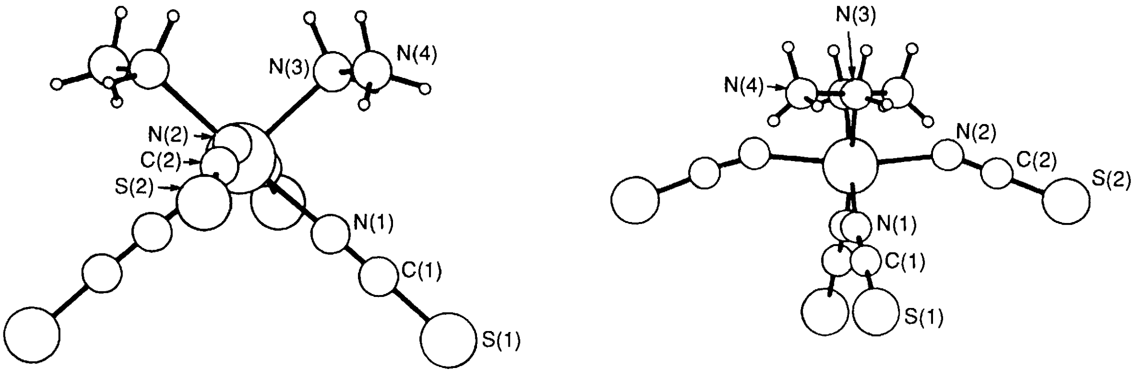
I



$$M{\diagup}\overline{N}{=}C{=}S$$

II

From the above it is obvious that the N–C bond distance in form **I** should be smaller than in the form **II**, whereas the C–S bond distance in **I** should be larger than in **II**. The values in Table 2 show a similar trend although some of the values fall in the same range within the 3σ limit. The Co–N bond distances, 2.091(6) Å in the linear and 2.098(7) Å in the angular Co–NCS linkages, are equal and are comparable to the similar bond lengths observed in many cobalt thiocyanate complexes.[35] The N–C–S angles in both cases are very close to 180° [178.4(8)° for



(a) (b)

Fig. 2 Structures of $[Co(N_2H_5)_2(NCS)_4]$ showing bent and linear Co–NCS bonds

Table 2 Fractional atomic coordinates for $(N_2H_5)_2Co(NCS)_4{\cdot}2H_2O$ with estimated standard deviations (e.s.d.s) in parentheses

Atom	x	y	z
Co	0.5	0.2906(2)	0.75
N(1)	0.6057(4)	0.1156(8)	0.7959(5)
C(1)	0.6620(5)	0.0177(8)	0.8103(5)
S(1)	0.7416(1)	−0.1264(2)	0.8327(2)
N(2)	0.4970(4)	0.3215(8)	0.9051(5)
C(2)	0.4859(4)	0.2687(8)	0.9806(5)
S(2)	0.4739(2)	0.1873(3)	0.0872(2)
N(3)	0.6077(4)	0.4908(8)	0.7962(5)
N(4)	0.6596(4)	0.4934(9)	0.9108(5)
O(w)	0.3223(4)	0.1334(12)	0.4439(6)

Table 3 Bond lengths (Å) and angles (°) in $(N_2H_5)_2Co(NCS)_4{\cdot}2H_2O$

Co–N(1)	2.091(6)	N(1′)–Co–N(3′)	83.4(2)
Co–N(2)	2.098(7)	N(2′)–Co–N(3)	83.8(2)
Co–N(3)	2.243(6)	N(2′)–Co–N(3′)	87.3(2)
N(1)–C(1)	1.146(9)	N(1)–Co–N(2)	95.9(3)
C(1)–S(1)	1.646(7)	N(1)–Co–N(2′)	92.5(3)
N(2)–C(2)	1.162(9)	N(1)–Co–N(3)	83.4(2)
C(2)–S(2)	1.627(8)	N(1)–Co–N(3′)	176.9(2)
N(3)–N(4)	1.445(8)	N(2)–Co–N(2′)	166.9(3)
		N(2)–Co–N(3)	87.3(2)
Co–N(1)–C(1)	173.2(6)	N(2)–Co–N(3′)	83.8(2′)
Co–N(2)–C(2)	151.9(6)	N(3)–Co–N(3′)	93.5(2)
Co–N(3)–N(4)	113.0(5)	N(1′)–Co–N(2)	92.5(3)
N(1)–C(1)–S(1)	178.4(8)	N(1′)–Co–N(2′)	95.9(3)
N(2)–C(2)–S(2)	177.2(7)	N(1′)–Co–N(3)	176.9(3)
N(1)–Co–N(1′)	99.7(3)		

Table 4 Hydrogen bonding in $(N_2H_5)_2Co(NCS)_4{\cdot}2H_2O$

D–H···A	D–A (Å)	D–H (Å)	A···H (Å)	D–H–A (°)
N(4)–H(41)···O(1)	2.703	0.985	1.724	172.5
N(4)–H(43)···S(1$^{\text{I}}$)	3.538	1.042	3.039	110.2
N(3)–H(32)···S(2$^{\text{II}}$)	3.764	1.056	2.821	148.8
O(1)–H(w2)···S(2$^{\text{III}}$)	3.517	0.895	3.063	113.5
N(3)–H(32)···S(2$^{\text{IV}}$)	3.447	1.056	2.881	113.8
N(4)–H(43)···S(2$^{\text{IV}}$)	3.292	1.042	2.408	142.0
O(1)–H(w1)···S(1$^{\text{V}}$)	3.437	0.821	2.869	128.1
N(3)–H(31)···S(1$^{\text{V}}$)	3.593	0.967	2.635	171.1
N(4)–H(43)···S(1$^{\text{VI}}$)	3.663	1.042	3.151	111.4

Symmetry codes: I $x, 1 + y, z$; II $x, 1 - y, -\frac{1}{2} + z$; III $\frac{1}{2} + x, \frac{1}{2} + y, z$; IV $1 - x, 1 - y, 2 - z$; V $\frac{3}{2} - x, \frac{1}{2} + y, \frac{3}{2} - z$; VI $= \frac{3}{2} - x, \frac{1}{2} - y, 2 - z$.

the linear and 177.2(7)° for the angular]. The presence of two kinds of NCS groups with different C–N bond lengths explains the observed doublet for ν(C–N) in the infrared spectra of the complexes.

No crystal structures of six-co-ordinated cobalt(II) complexes containing terminal NCS ligands are known.[35,36] However, in other cobalt complexes containing terminal NCS ligands the Co–N–C angle ranges from 155 to 175°.[35,36] The unique feature of the present structure is the existence of both bent and linear Co–NCS forms in the same molecule (Fig. 2). Another significant feature is that the two hydrazinium cations are in *cis* positions unlike the *trans* co-ordination observed in chloride[18] and sulphate complexes.[9,10] This is the first example in which the hydrazinium cations are in *cis* positions. The longer bond distance of 2.243(6) Å observed for Co–N(3) compared to the value of 2.114(9) Å in $[Co(NH_3)_6]Cl_2$[37] indicates a weaker metal–nitrogen interaction. The N–N bond length of 1.445(8) Å observed in the present structure is comparable to the values in other hydrazinium complexes. The Co–N(3)–N(4) angle is 113.0(5)°, similar to the value of 110° found in the zinc complex,[8] but apparently smaller than the 119.1(3)° observed in the copper complex.[17]

The two water molecules in the structure are located in the vicinity of NH_3^+ of the $N_2H_5^+$ ions, held together by N–H···O type hydrogen bonds. The sulphur atoms are also involved in N–H···S and O–H···S hydrogen bonding (Table 4).

Structure of $(N_2H_5)_2Ni(NCS)_4{\cdot}2H_2O$.—Preliminary studies on single crystals of the nickel complex indicate that it crystallizes in the same space group as that of the cobalt complex. The unit-cell parameters obtained from these studies are: $a = 16.4$, $b = 7.7$, $c = 13.1$ Å, $\beta = 112.0°$, $U = 1534$ Å^3, $Z = 4$, $D_m = 1.67$ g cm^{-3} and $D_c = 1.70$ g cm^{-3}. These data, coupled with spectral data, confirm that the nickel complex is isostructural with the cobalt complex.

Acknowledgements

The authors are grateful to Professor H. Manohar for valuable discussions and interest.

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Received 14*th November* 1990; *Paper* 0/05119E