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Di-Cobalt(II) Complexes of a Macrocyclic Ligand containing Nitrogen Atom-Only Thiocyanate, Selenocyanate and 1,1-Azide Bridges: X-Ray Structures of the μ-(thiocyanato-N)-μ-ethoxo and μ-(1,1-azido)-μ-methoxo Derivatives

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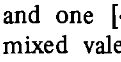
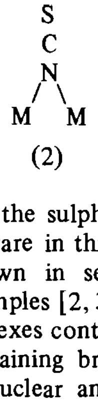
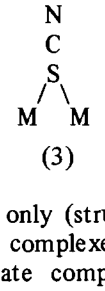
The thiocyanate and selenocyanate ions are well known to coordinate to metal ions either *via* the nitrogen atom or *via* the sulphur (or selenium) atom [1]. There are also very numerous instances where these ions act as bridges between adjacent metal ions involving bonding of the nitrogen atom to one metal and sulphur (or selenium) to the other (structure (1)) [1]. In contrast, bridging *via* the nitrogen atom only (structure (2)) or the sulphur atom only (structure (3)) is extremely rare in thiocyanate complexes and apparently unknown in selenocyanate complexes. There are two examples [2, 3] of structurally defined thiocyanate complexes containing bridging mode (2) and one [4] containing bridging mode (3). In the mixed valence dinuclear anion $[Re_2(NCS)_{10}]^{3-}$ the two metal atoms are bridged *via* the nitrogen atoms of two of the thiocyanate ions [2]. Nitrogen atom-only thiocyanate bridges also occur in the complex $[Cd_2(NCS)_4(butrz)_3]_\infty$ (butrz = 4-t-butyl-1,2,4-triazole) which consists of chains of Cd(II) ions linked alternatively by triazole and N(CS) bridges [3]. The unique example [4] of bridging mode (3) occurs in the di-Cu(I) complex $[Cu_2L(SCN)_2]$ of the macrocyclic ligand L [structure (4)] in which each tetrahedrally coordinated Cu(I) ion is bonded to two nitrogen atoms of the macrocycle and two (bridging) thiocyanate sulphur atoms. An analogous selenocyanato complex $(Cu_2L(SeCN)_2)$ containing two selenium atom bridges has also been prepared [5]. Both μ-1,3 and μ1,1 bridging modes are known for the azide ion, the former being the more common [6].



(1)



(2)



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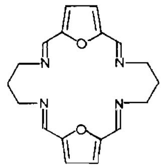

(4)

The unusual bridging thiocyanate modes (2) and (3) in two of the above examples can reasonably be associated with the imposed close proximity of the metal centres which precludes the formation of the lengthways bridge (1). In $[Re(NCS)_{10}]^{3-}$ the metal ions are held at a separation of *ca.* 2.61 Å by a metal–metal bond [2], while in $[Cu_2L(SCN)_2]$ it is the small cavity size of the macrocycle that is responsible for the small Cu···Cu separation (2.796(8) Å) [4]. The choice of sulphur as the bridging atom in this complex is presumably determined by the 'soft' (class b) character of Cu(I). It was of interest to attempt the preparation of bimetallic complexes of the same ligand L containing N-bonded only NCS^- bridges by changing to a metal ion of predominantly 'hard' (class a) character. We here report some di-cobalt(II) complexes containing intramolecular thiocyanate, selenocyanate and azide bridges along with the crystal and molecular structures of two of these complexes.

The following complexes were examined: $(Co_2L(OMe)(NCS)_3)$. $(Co_2L(OEt)(NCS)_3)$, $(Co_2L(OEt)(NCSe)_3)$ and $Co_2L(OMe)(N_3)_3)$. Details of the syntheses will be given in a forthcoming publication describing a wider range of di-cobalt(II) complexes of this macrocycle. Early indications that the thiocyanates and selenocyanate might contain nitrogen atom bridges were provided by the IR spectra (*vide infra*). The structures of $(Co_2L(OEt)(NCS)_3)$ (I) and $(Co_2L(OMe)(N_3)_3)$ (II) were determined by single crystal X-ray diffraction methods.

Crystal data for both complexes are given in Table I. The crystals were mounted in turn on a Stoe STADI 2 diffractometer and data were collected *via* variable width *w* scan. Both structures were solved by the Patterson method and the positions of non-hydrogen atoms found from the Fourier syntheses. Both structures showed features of disorder. In (I), there was disorder in the bridging atoms and the saturated part of the macrocycle. In the bridge between cobalt atoms across the centre of symmetry there were two different groups –OEt and –NCS. Each group was given 50% occupancy. The bridging atom itself was given a scattering factor of 0.5 (O + N). Two distinct positions were observed for the two carbons bonded to this atom and these were refined with 50% occupancy as were the terminal $-CH_3$ and S moieties. It proved necessary to constrain the

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TABLE I. Crystal Data and Refinement Details.

	(I)	(II)
Formula	$Co_2L(OEt)(NCS)_3$ $Co_2S_3N_7O_3C_{23}H_{25}$	$Co_2L(OMe)(NNN)$ $Co_2N_{13}O_3C_{19}H_{23}$
M	661.2	599.0
Class	Monoclinic	Monoclinic
Spacegroup	$P2_1/c$	$P2_1/n$
a (Å)	9.03(1)	8.381(7)
b (Å)	10.73(1)	10.09(1)
c (Å)	14.64(1)	14.185(11)
β (deg)	99.0(1)	96.1(1)
U (Å^3)	1401.0	1192.7
Z	2	2
Radiation	Mo-K_α	Mo-K_α
2* theta max (deg)	40	40
No. of data measured	1369	1334
Criteria for data inclusion	$I > 1.5\sigma(I)$	$I > 1.5\sigma(I)$
No of data used in refinement	692	700
R	0.087	0.093
R_w	0.092	0.095

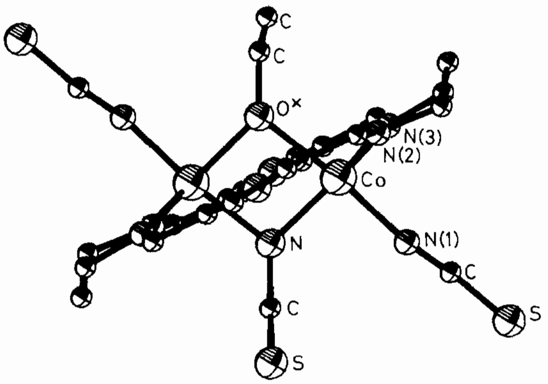

Fig. 1. An ordered molecule of ($Co_2L(OEt)(NCS)_3$) (I).

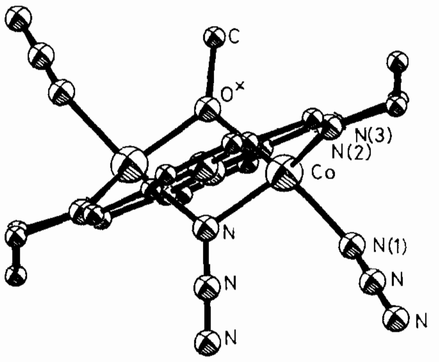

Fig. 2. An ordered molecule of ($Co_2L(OMe)(N_3)_3$) (II).

O–C and N–C distances. The situation in (II) was also complicated. The disordered bridging groups this time are –NNN and –OMe. As in (I) we could not see any disorder in the bridging atom position and this refined with occupancy 0.5 (O + N). The second atom when refined as one atom converged at a position 1.32(3) Å from the bridging atom. This distance is *ca.* halfway between a O–C and N–N bond. We then separated this peak into two, constraining the bond lengths, and this model refined. The third atom should be 0.5*N but the peak was very elongated. We separated it into two and refined each position as 0.25*N. This complete model converged successfully. In this molecule the macrocycle ring was ordered.

The two molecules (I) and (II) are shown in Figs. 1 and 2, respectively. Both are disordered centrosymmetric structures with two cobalt atoms enclosed within the macrocycle I. In the Figures we show one possible orientation of each molecule. In both structures the cobalt atoms are five-coordinate with a distorted trigonal bipyramidal environment (Table II). Each metal atom is bonded to two nitrogen atoms N(2), N(3) of the macrocycle and a disordered N/O bridge atom in the equatorial plane. The two axial sites are occupied by N(1) from a terminal anion (NCS in (I) and NNN in (II)) and the other disordered N/O bridge atom (called N/O^x in Table II). Despite the disorder it seems clear the equatorial bridge bonds Co–N/O (mean 1.985 Å) are significantly shorter

TABLE II. Selected Bond Distances (Å) and Angles (°) in (I) and (II).

	(I)	(II)
Co–N(1)	2.043(20)	2.042(20)
Co–N(2)	2.050(29)	2.077(17)
Co–N(3)	2.23(4)	2.109(15)
Co–O/N^x	2.109(16)	2.135(17)
Co–O/N	1.975(19)	1.996(17)
Co···Co	3.116(4)	3.196(6)
N(1)–Co–N(2)	89.1(9)	88.7(7)
N(1)–Co–N(3)	89.7(11)	93.5(6)
N(1)–Co–O/N^x	173.1(8)	173.8(7)
N(1)–Co–O/N	93.1(7)	96.1(8)
N(2)–Co–N(3)	90.8(7)	99.7(7)
N(2)–Co–O/N^x	93.4(6)	92.4(6)
N(2)–Co–O/N	135.9(6)	131.9(5)
N(3)–Co–O/N^x	96.6(7)	92.3(6)
N(3)–Co–O/N	133.2(14)	127.6(6)
O/N–Co–O/N^x	80.6(7)	78.7(6)

than the axial bridge bonds Co–N/O^x (mean 2.122 Å). In both the structures the furan oxygen atoms are unbonded at *ca.* 3.0 Å from the metal. The Co··· Co separation is 3.116(4) Å in (I) and 3.196(6) Å in (II).

Physical properties (Table III) of the complexes are very similar and show that ($Co_2L(OMe)(NCS)_3$) and ($Co_2L(OEt)(NCSe)_3$) have analogous structures. The two thiocyanato complexes and the selenocyanate showed two strong absorptions in the 1950–2100 cm^{-1} region of the IR spectra. The more intense band at 2070–2080 cm^{-1} is assigned to the asymmetric stretch (mainly C≡N) of the terminally bound groups, while the less intense band at 1990–2000 cm^{-1}, together with a shoulder on the low frequency side, is assigned to ν_{asym} of the bridging group. The occurrence of the latter band at frequencies at or below 2000 cm^{-1} has been noted previously [2, 3] and will likely prove to be a useful diagnostic spectral feature of this bridging mode. The asymmetric stretch of the azide ion in ($Co_2L(OMe)(N_3)_3$) appears as a doublet at 2045 and 2068 cm^{-1}. While assignment is more difficult in this case earlier studies [7] on di-Cu(II) complexes of a related macrocycle suggest that μ-1,1-azido groups absorb at slightly higher frequencies than terminally bonded azide.

Room temperature magnetic moments (Table III) fall between 4.7–5.1 B.M. and show only relatively small dependences on temperature in the range 90–300 K. For the case of ($Co_2L(OMe)(N_3)_3$) a small ferromagnetic effect is indicated by an increase in μ_{eff} on cooling. A similar ferromagnetic interaction, with the ground spin triplet state stabilised by 70 ± 20 cm^{-1} with respect to the singlet, has recently been reported for a di-μ-1,1-azido-di-Cu(II) complex [6c].

Solid state electronic spectra (Table III) are typical for high spin Co(II) in trigonal bipyramidal environments [8]. The close similarity of the spectra of the different complexes is strong evidence for a common structural framework comprising one nitrogen atom – only pseudohalide bridge and one alkoxo bridge between the metal centres. The occurrence of two different bridging groups in these complexes was unexpected and the reason is not yet understood. A di-copper(II) complex of the same macrocycle contains two alkoxo bridges and two terminally bonded thiocyanate groups [9].

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TABLE III. Analytical, Spectroscopic and Magnetic Data for the Complexes.

Complex	Analysis (%)			ν_{asym} of pseudohalide (cm^{-1})	Electronic^b spectra (cm^{-1})	μ_{eff}/B.M.^{c}	
	C	H	N			(293 K)	(93 K)
$Co_2L(OMe)(NCS)_3$	40.6(40.8)	3.6(3.6)	15.0(15.1)	2075, 2000	20,200, 18,400, 16,200, 13,200, 10,400	5.10	4.88
$Co_2L(OEt)(NCS)_3$	41.8(41.8)	3.8(3.8)	14.7(14.8)	2080, 2000	20,200, 18,400 16,300, 13,300, 10,400	4.72	4.67
$Co_2L(OEt)(NCSe)_3$	34.5(34.4)	3.2(3.1)	12.0(12.2)	2070, 1995	20,300, 18,100 16,600, 13,000	5.10	5.04
$Co_2L(OMe)(N_3)_3$	38.1(38.1)	3.9(3.9)	30.4(30.4)	2068, 2045	19,500, 17,000, 15,900, 12,500, 9,600	5.11	5.31

^{a}Calculated values in parenthesis. ^{b}Solid state spectra. ^{c}Corrected for diamagnetism of ligands.

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