Crystal and Molecular Structure of a Cobalt(III) Macrocyclic Complex: *trans*-Di-isothiocyanato-*N*-*rac*-(5,12-dimethyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene)cobalt(III) Thiocyanate Monohydrate

By **Roderic J. Restivo, Janice Horney,** and **George Ferguson,*** Chemistry Department, University of Guelph, Guelph, Ontario, Canada N1G 2W1

Crystals of the title compound are monoclinic, space group $P2_1/c$, with $Z = 4$ in a unit cell of dimensions a = 8.932(2), b = 15.573(5), c = 17.022(4) Å, β = 110.60(1)°. The structure was solved by the heavy-atom method and refined by block-diagonal least-squares calculations to R 0.075 for 1 049 observed reflexions measured on a diffractometer. The cation has octahedral co-ordination with *trans*-isothiocyanato-groups, a *trans*-arrangement of imine (and secondary amine) moieties, with the N–H bonds of the secondary amine groups in a *cis*-orientation. Principal mean bond lengths are Co–N(SCN) 1.89(1), Co–N(H) 1.98(1), and Co–N(imine) 2.01(1) Å. The crystal contains thiocyanate ions (which may be disordered) [C–N 1.01(3) and C–S 1.58(2) Å], water molecules, and both D and L racemic forms of the cation, separated by normal distances.

OUR interest in the stereochemistry of cobalt(III) macrocyclic complexes has been prompted by recent work [1] on the preparation of transition-metal complexes of the macrocyclic ligand deduced to be 5,12-dimethyl-1,4,8,11-tetra-azacyclotetra-4,11-diene, hereafter Me_2-[14]diene.[2,3] A number of metal(II) complexes [M(Me_2-[14]diene)][ClO_4]$_2$ (M = Ni, Cu, Co, or Zn) with the poorly co-ordinating perchlorate anion have been prepared and a series of octahedral cobalt(III) complexes of the sug-

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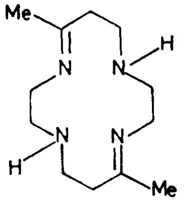
[1] R. W. Hay and G. A. Lawrance, *J.C.S. Dalton*, 1975, 1466, 1566.

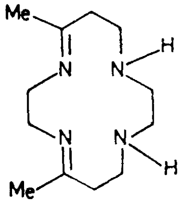
[2] R. A. Kolinski and B. Korybut-Daskiewicz, *Bull. Acad. Pol. Sci.*, 1969, **17**, 13.

[3] Under the system of abbreviations for macrocyclic ligands given by V. L. Goedken, P. H. Merrell, and D. H. Busch, *J. Amer. Chem. Soc.*, 1972, **94**, 3397, the ligand should be abbreviated to Me_2[14]dieneN_4; however, we have chosen to follow the usage of ref. 1, *i.e.* Me_2[14]diene.

gested type *trans*-[Co(Me$_2$[14]diene)L$_2$]$^{n+}$ (L = Cl$^-$, Br$^-$, NO$_2$$^-$, SCN$^-$, or NH$_3$) and *cis*-[Co(Me$_2$[14]diene)Y]$^{n+}$ (Y = CO$_3$$^{2-}$ or acetylacetonate) have been synthesized.[1] On co-ordination to the metal ion, two types of stereoisomers are possible, depending upon the relative orientation of the secondary-amine N–H bonds in Me$_2$[14]diene; a *meso*-form with a *trans*-arrangement of N–H groups or a racemic mixture of the optically active form with *cis*-N–H groups. Hinz and Margerum [4] refer to the reduction product of Me$_2$[14]diene, *viz.* Me$_2$[14]ane, and write a C-*meso*-structure for it. To confirm the correctness of the Me$_2$[14]diene formulation with the transoid arrangement (I) rather than the 7,12-dimethyl cisoid structure (II), and also to determine precise details of the stereochemistry of these complexes, we have therefore examined a number of the derivatives and report here the results of an *X*-ray investigation of the [Co(Me$_2$[14]diene)(NCS)$_2$][SCN]·H$_2$O structure.



(I)



(II)

EXPERIMENTAL

Dark red needle-shaped crystals of [Co(Me$_2$[14]diene)(NCS)$_2$][SCN]·H$_2$O suitable for *X*-ray analysis, were obtained by slow evaporation from isopropyl alcohol. A crystal *ca.* 0.20 × 0.14 × 0.07 mm was chosen for data collection.

Crystal Data.—C$_{12}$H$_{26}$CoN$_7$OS$_3$, $M = 475.5$, Monoclinic, $a = 8.932(2)$, $b = 15.573(5)$, $c = 17.022(4)$ Å, $\beta = 110.60(1)°$, $U = 2\,217.8$ Å^3, $D_m = 1.42(1)$, $Z = 4$, $D_c = 1.424$, $F(000) = 992$. Mo-K_α radiation, $\lambda = 0.710\,69$ Å; μ(Mo-K_α) = 10.95 cm^{-1}. Systematic absences: $0k0$, $k = 2n + 1$ and $h0l$, $l = 2n + 1$ indicate space group $P2_1/c$ (C_{2h}^5, No. 14) uniquely.

Intensity data were measured as described previously [5] on a Hilger and Watts Y 290 computer-controlled diffractometer by use of the θ—2θ scanning technique with graphite-monochromated Mo-K_α radiation to $\theta_{max.}$ 20°. The 2 076 independent intensities obtained were corrected for Lorentz and polarization factors but not for absorption (which in any case is small: μ_R 0.86—0.93). 1 049 Reflexions having $I > 3\sigma(I)$ were considered observed and used in the solution and refinement of the structure.

Structure Analysis.—The structure was solved by the heavy-atom method and refined by least-squares procedures, initially with isotropic and finally with anisotropic thermal parameters, a block-diagonal approximation to the least-squares matrix, and a weighting scheme $\sqrt{w} = 1/[\sigma^2(F) + 2 \times 10^{-3}F^2]^{1/2}$. A difference-Fourier synthesis revealed electron-density concentrations (largest value 0.85 eÅ^{-3}) in chemically reasonable positions for some (including the two hydrogens of the secondary-nitrogen groups) but not all

TABLE 1

Atomic positional parameters (× 10^4)

Atom	*x*	*y*	*z*
Co	1 680(2)	2 042(1)	2 070(1)
S(1)	3 977(6)	0 129(3)	0 743(3)
S(2)	−0 689(7)	3 954(4)	3 371(4)
S(31)	7 965(10)	0 607(6)	4 942(6)
N(1)	0 024(16)	2 240(9)	0 953(8)
N(4)	2 990(17)	2 944(10)	1 779(9)
N(8)	3 324(15)	1 880(9)	3 190(8)
N(11)	0 364(20)	1 174(12)	2 418(12)
N(21)	2 630(15)	1 188(8)	1 608(8)
N(22)	0 735(14)	2 891(9)	2 534(8)
N(31)	6 661(27)	1 794(13)	5 535(11)
C(2)	0 796(23)	2 560(12)	0 360(11)
C(3)	1 858(26)	3 333(14)	0 834(12)
C(5)	4 195(31)	3 275(20)	2 137(22)
C(6)	5 158(22)	2 869(17)	2 968(12)
C(7)	4 941(21)	1 980(12)	3 182(12)
C(9)	3 091(22)	1 003(12)	3 504(12)
C(10)	1 335(22)	0 896(13)	3 399(10)
C(12)	−0 906(29)	0 862(17)	2 127(20)
C(13)	−1 773(22)	1 153(15)	1 196(10)
C(14)	−0 921(22)	1 438(12)	0 626(11)
C(15)	4 738(23)	4 094(12)	1 767(13)
C(16)	−1 784(24)	0 344(15)	2 587(13)
C(21)	3 214(18)	0 729(10)	1 250(9)
C(22)	0 146(18)	3 327(10)	2 865(9)
C(31)	7 105(22)	1 268(13)	5 349(12)
O	3 810(18)	2 937(12)	4 652(10)

TABLE 2

Intramolecular distances (Å) and angles (°) with estimated standard deviations in parentheses

(*a*) In the cation			
(i) Distances			
Co–N(1)	1.98(1)	C(7)–N(8)	1.46(2)
Co–N(4)	2.00(2)	N(8)–C(9)	1.51(2)
Co–N(8)	1.97(1)	C(9)–C(10)	1.52(3)
Co–N(11)	2.01(2)	C(10)–N(11)	1.65(2)
Co–N(21)	1.89(1)	N(11)–C(12)	1.17(3)
Co–N(22)	1.88(1)	C(12)–C(13)	1.57(3)
N(1)–C(2)	1.50(3)	C(12)–C(16)	1.52(4)
C(2)–C(3)	1.57(3)	C(13)–C(14)	1.50(3)
C(3)–N(4)	1.68(2)	C(14)–N(1)	1.50(2)
N(4)–C(5)	1.15(3)	N(21)–C(21)	1.17(2)
C(5)–C(6)	1.51(4)	C(21)–S(1)	1.58(2)
C(5)–C(15)	1.57(4)	N(22)–C(22)	1.13(2)
C(6)–C(7)	1.46(3)	C(22)–S(2)	1.64(2)
(ii) Angles			
N(1)–Co–N(4)	87.5(6)	Co–N(4)–C(5)	134.5(20)
N(1)–Co–N(8)	178.4(9)	N(4)–C(5)–C(6)	115.2(28)
N(1)–Co–N(11)	94.1(6)	N(4)–C(5)–C(15)	120.8(25)
N(1)–Co–N(21)	90.2(6)	C(6)–C(5)–C(15)	124.0(20)
N(1)–Co–N(22)	90.0(6)	C(5)–C(6)–C(7)	123.2(18)
N(4)–Co–N(8)	91.6(6)	C(6)–C(7)–N(8)	108.8(15)
N(4)–Co–N(11)	176.8(8)	C(7)–N(8)–C(9)	111.2(13)
N(4)–Co–N(21)	90.2(7)	Co–N(8)–C(7)	112.4(11)
N(4)–Co–N(22)	89.9(7)	Co–N(8)–C(9)	108.1(9)
N(8)–Co–N(11)	86.7(6)	N(8)–C(9)–C(10)	108.8(14)
N(8)–Co–N(21)	91.2(6)	C(9)–C(10)–N(11)	104.1(16)
N(8)–Co–N(22)	88.6(5)	C(10)–N(11)–C(12)	113.9(23)
N(11)–Co–N(21)	92.6(7)	Co–N(11)–C(10)	108.8(11)
N(11)–Co–N(22)	87.4(7)	Co–N(11)–C(12)	137.2(20)
N(21)–Co–N(22)	179.9(18)	N(11)–C(12)–C(13)	111.6(26)
C(14)–N(1)–C(2)	111.0(14)	N(11)–C(12)–C(16)	127.0(27)
Co–N(1)–C(2)	109.6(10)	C(13)–C(12)–C(16)	120.9(18)
Co–N(1)–C(14)	111.1(10)	C(12)–C(13)–C(14)	124.0(17)
N(1)–C(2)–C(3)	104.1(15)	C(13)–C(14)–N(1)	110.8(16)
C(2)–C(3)–N(4)	105.6(15)	Co(1)–N(21)–C(21)	172.1(13)
C(3)–N(4)–C(5)	118.6(22)	N(21)–C(21)–S(1)	178(2(14)
Co–N(4)–C(3)	106.4(11)	Co(1)–N(22)–C(22)	172.3(14)
		N(22)–C(22)–S(2)	178.7(14)
(*b*) In the anion			
(i) Distances			
N(31)–C(31)	1.01(3)	C(31)–S(31)	1.58(2)
(ii) Angle			
N(31)–C(31)–S(31)	166.2(25)		

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[4] F. P. Hinz and D. W. Margerum, *Inorg. Chem.*, 1974, **13**, 2941.

[5] See *e.g.* G. Ferguson, P. A. Gunn, W. C. Marsh, R. McCrindle, R. Restivo, J. D. Connolly, J. W. B. Fulke, and M. S. Henderson, *J.C.S. Perkin I*, 1975, 496.

the hydrogen positions, and showed no other chemically recognizable features. No allowance was made for hydrogen-atom contributions in any of the calculations, which were carried out on the University IBM 370/155 computer system by use of locally-modified programs for data-handling and the '*X*-Ray '72' system.[6a] Scattering factors from ref. 6*b* were used throughout the refinement and anomalous dispersion corrections were included for the cobalt atom.[7] The final *R* was 0.075, and *R'* 0.089, where $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w(F_o^2)]^{1/2}$. The estimated standard deviation of an obervation of unit weight was 1.2. Observed and calculated structure factors, thermal parameters, and details of mean plane calculations are listed in Supplementary Publication No. SUP 21482 (22 pp., 1 microfiche).*

Atomic co-ordinates are listed in Table 1 and bond lengths and angles in Table 2.

DISCUSSION

The principal interest in the structure lies in the stereochemistry of the complex cation (Figure 1) which contains cobalt(III) octahedrally co-ordinated to the secondary amino- and imino-nitrogen atoms of $Me_2[14]$diene in approximately planar *trans*-co-ordination; the octahedron is completed by nitrogen atoms of the *trans*-isothiocyanate ligands. Calculation of some weighted least-squares planes established the overall planarity of the macrocycle as well as the local planarity about the imine double-bonds. The results show that the four nitrogen atoms of the quadridentate ligand deviate significantly (0.02—0.05 Å) from coplanarity. The *trans*-positions of the imine groups [indicated by the shorter C=N distances, mean 1.16(1) Å], the near planarity of the C(3), N(4), Co, C(5), C(6), C(15), and C(10), N(11), Co, C(12), C(13), C(16) moieties, and the bond angles at N(4), C(5), N(11), and C(12), the tetrahedral-like environment at N(1) and N(8), and the unambiguous location of the methyl groups, identifies the cation as [Co-(*trans*-$Me_2[14]$diene)$(NCS)_2]^+$. The appropriate tetrahedral co-ordination about the secondary nitrogen atoms (Figure 1) also clearly positions both hydrogen atoms above the ligand plane. This further identifies the complex as [Co{*N-rac-trans*-$Me_2[14]$diene}$(NCS)_2]^+$; the space group ensures that the crystal is a racemate containing equal numbers of both enantiomers. There is an approximate two-fold symmetry axis coinciding with the SCN–Co–NCS axis, as a result of the two secondary N–H bonds being oriented on the same side of the CoN_4(ligand) plane.

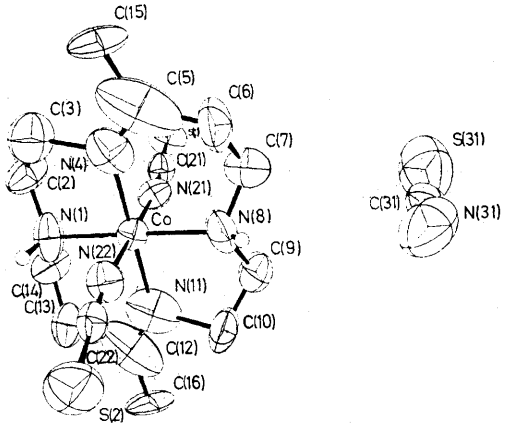

FIGURE 1 An ORTEP drawing of the cation and anion, showing atomic numbering and vibration ellipsoids at the 50% probability level

The Co–N(macrocycle) bond lengths [means Co–N(H) 1.98(1), Co–N(imino) 2.01(1) Å] are not significantly different and may be compared with similar bond lengths in *e.g. trans*-[Co(*meso-cis*-[14]diene)$(CN)_2][ClO_4]$ where Co–N(H) is 1.96, 1.99 Å and Co–N(imino) is 1.92, 1.96 Å.[8] The thermal ellipsoids (Figure 1) show abnormally large motion of the carbon atoms C(5) and C(12) bonded to the imino-nitrogen atoms and it is possible that there is some disorder associated with these portions of the molecule which would lead to the abnormal values observed for bond lengths in these areas [C(sp^3)–N(imino) 1.67(2), C(sp^2)–N(imino) 1.16(3) Å]. None of the other atoms in the cation appear to have abnormally large thermal vibration and the ligand bonds C(sp^3)–N(H) [mean 1.49(2) Å] and C(sp^3)–C(sp^3) [mean 1.51(5) Å] are close to values normally observed for macrocyclic ring complexes.[9]

The precise conformation adopted by the ligand is best described in terms of the various torsion angles (Figure 2). Maximum torsional strain occurs at C(9)–C(10), C(5)–C(6), and C(13)–C(14) (49, 23, 68°; strain-free values 60, 30, 60°); these values indicate the presence of strain at the methylene carbon atoms of the six-membered ring. Bond-angle strain is also apparent in the six-membered chelate rings. The angles C(5)–C(6)–C(7) [123.2(18)°] and C(12)–C(13)–C(14) [124.0(17)°], and angles Co–N(4)–C(5) [134.5(20)°] and Co–N(11)–C(12)

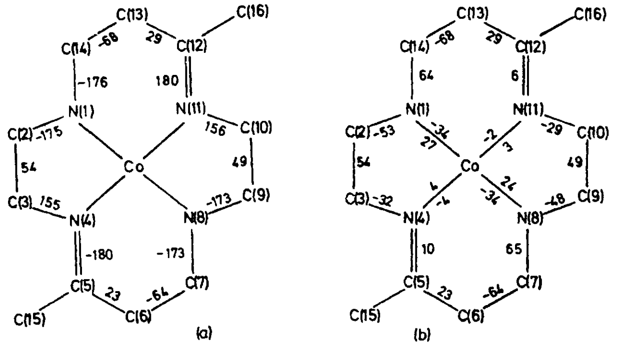

FIGURE 2 Torsion angles (°) for the cation: (a) within the macrocycle and (b) within the five- and six-membered rings

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* See Notice to Authors No. 7, in *J.C.S. Dalton*, 1975, Index issue.

[6] (*a*) '*X*-Ray' System of Computing Programs, Report TR 192. Computing Science Center, University of Maryland, version of June 1972; (*b*) D. Cromer and J. Mann, *Acta Cryst.*, 1968, 321.

[7] D. T. Cromer, *Acta Cryst.*, 1965, **18**, 17

[8] P. R. Ireland and W. T. Robinson, *J. Chem. Soc.* (*A*), 1970, 663.

[9] (*a*) N. F. Curtis, D. A. Swann, and T. N. Waters, *J.C.S. Dalton*, 1973, 1408; (*b*) D. A. Swann, T. N. Waters, and N. F. Curtis, *ibid.*, 1972, 1115; (*c*) F. Hanic and D. Miklos, *J. Cryst. Mol. Struct.*, 1972, **2**, 115; (*d*) N. F. Curtis, *Co-ordination Chem. Rev.*, 1968, **3**, 3; (*e*) L. F. Lindoy and D. H. Busch, 'Preparative Inorganic Reactions,' ed. W. L. Jolly, vol. 6, Wiley–Interscience, New York, 1971, p. 1.

[137.2(20)°] have major deformations when compared to the appropriate strain-free values (109.5 and 120°). Similar distortions occur at analogous positions in related diene macrocycles: 119 and 131° in *rac*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetra-azacyclotetradeca-4,11-dienenickel(II) perchlorate,[10] [Ni(*rac-trans*-[14]diene)][ClO$_4$]$_2$, and 115 and 126° in dicyano-5,7,7,12,12,14-hexamethyl-1,4,8,11-tetra-azacyclotetradeca-4,14-dienecobalt(III) perchlorate,[8] *trans*-[Co(*meso-cis*-[14]diene)(CN)$_2$][ClO$_4$]. The suggestion of Bailey and Maxwell,[10] that enlargement of these angles in the latter two complexes is probably due to the accumulated strain in the six-membered ring caused by the presence of the imine group, is also applicable here.

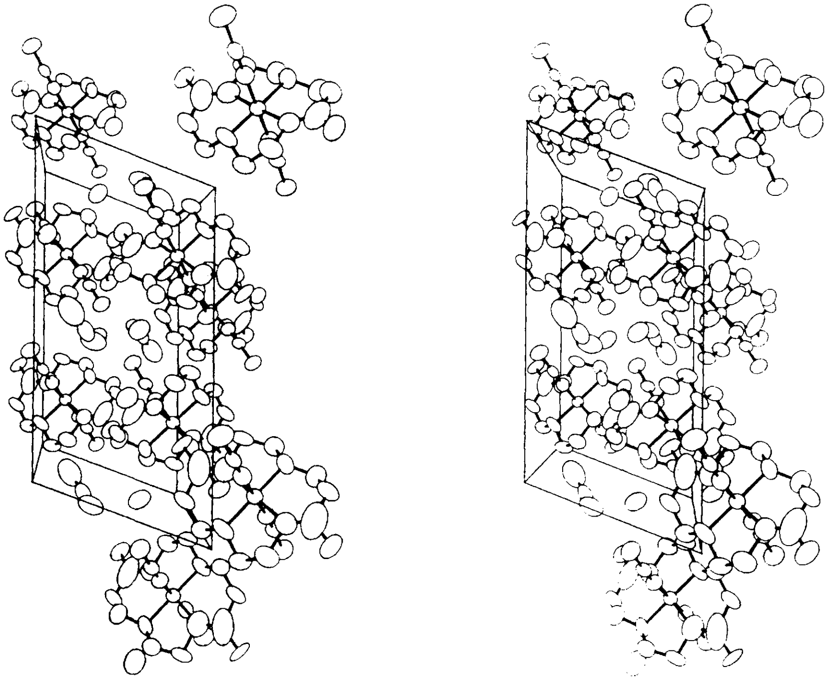

FIGURE 3 Stereoview of the lattice as viewed along the *b* axis

The conformation of the six-membered rings in the present complex may be described as a ' sofa ' form [compare the distribution of torsion angles (Figure 2b) with theoretical values].[11] The accumulated strain caused by the presence of the imine group is believed to be the cause of this distortion from the more energetically favourable chair form.[11] It has been pointed out [10] that there is considerably less strain in the six-membered chelate-ring conformation of *trans*-[Co(*meso-cis*-[14]diene)(CN)$_2$]$^+$ where it was considered more energetically favourable to relax the mirror-plane condition and thereby reduce torsional strain. The five-membered rings formed by the ethylenediamine residues and the Co atom have a highly asymmetrical *gauche* (or near-envelope) conformation, which has been predicted [12] for planar co-ordination of the macrocycle (including *trans*-disubstituted co-ordination) when the hydrogen atoms on the included nitrogen atoms are *cis*.

The bond distances in the co-ordinated isothiocyanato-ligands [means C–N 1.15(2) and C–S 1.61(3) Å] are similar to values obtained for the isothiocyanato-group in *cis*-[Pt(NCS)(SCN)(Ph$_2$PC$\equiv$CBu^t)$_2$] [1.11(4) and 1.60(3) Å].[13] It is possible that the free thiocyanate ion in the present structure may be disordered, as judged by the large anisotropic motion of its atoms (Figure 1) and by the observed geometry [C–N 1.01(3), C–S 1.58(2), N–C–S 166(3)°]; somewhat similar values have been reported for the SCN$^-$ ion in [Ni(Me$_6$[14]diene)][SCN]$_2$·H$_2$O [C–N 1.14(2) and C–S 1.61(1) Å; N–C–S 175°].[9c]

The crystal structure consists of monomeric [Co(Me$_2$-[14]diene)(NCS)$_2$]$^+$ cations, [SCN]$^-$ anions, and water molecules held together by electrostatic forces, van der Waals interactions, and weak hydrogen bonds. Figure 3 is a stereoview of the ionic packing within the unit cell as viewed down the shortest axis. All intermolecular contacts <3.5 Å were calculated; there is possibly a weak hydrogen bond between the oxygen atom of the water molecule and the nitrogen atom of the free thiocyanate group, O···N(31) 3.04(3) Å. There are no other unusually short contacts present.

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[5/703 *Received*, 14*th April*, 1975]

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[10] M. F. Bailey and I. E. Maxwell, *J.C.S. Dalton*, 1972, 938.

[11] C. Altona, H. J. Geise, and C. Romers, *Tetrahedron*, 1967, **23**, 439; 1968, **24**, 13.

[12] P. O. Whimp, M. F. Bailey, and N. F. Curtis, *J. Chem. Soc.* (*A*), 1970, 1956.

[13] Y. S. Wong, S. Jacobson, P. C. Chieh, and A. J. Carty, *Inorg. Chem.*, 1974, **13**, 284.