

This work was supported by a Hong Kong RGC Earmarked Grant for Research (Acc. No. 221600010).

References

- BATTAGAGLIA, L. P., CORRADI, A. B., MENABUE, L., SALADINI, M., SOLA, M. & GAVIOLI, G. B. (1985). *Inorg. Chim. Acta*, **107**, 73–79.
- BERGMAN, J. G. & COTTON, F. A. (1966). *Inorg. Chem.* **5**, 1420–1428.
- CHEN, X.-M. & MAK, T. C. W. (1991a). *J. Chem. Soc. Dalton Trans.* pp. 1219–1222.
- CHEN, X.-M. & MAK, T. C. W. (1991b). *J. Crystallogr. Spectrosc. Res.* **21**, 471–478.
- CLEGG, W., LACY, O. M. & STRAUGHAN, B. P. (1987). *Acta Cryst.* **C43**, 794–797.
- FISCHER, M. S., TEMPLETON, D. H. & ZALKIN, A. (1970). *Acta Cryst.* **B26**, 1392–1397.
- KENNARD, C. H. L., SMITH, G., O'REILLY, E. J. & MANOHARAN, P. T. (1984). *Inorg. Chim. Acta*, **82**, 35–40.
- MEHROTRA, R. C. & BROHRA, R. (1983). *Metal Carboxylates*. New York: Academic Press.
- NADZHAFOV, G. N., SNULIN, A. N. & MAMEDOV, KH. S. (1981). *J. Struct. Chem.* **22**, 898–902.
- NIEKERK, J. N. VAN & SCHOENING, F. R. L. (1953). *Acta Cryst.* **6**, 609–612.
- RAVIKUMAR, K., RAJAN, S. S., NATARAJAN, S., PONNUSWAMY, M. N. & TROTTER, J. (1985). *Z. Kristallogr.* **171**, 201–207.
- SHELDRIK, G. M. (1982). *Computational Crystallography*, edited by D. SAYRE, pp. 506–514. Oxford Univ. Press.
- SHELDRIK, G. M. (1985). *Crystallographic Computing 3: Data Collection, Structure Determination, Proteins and Databases*, edited by G. M. SHELDRIK, C. KRÜGER & R. GODDARD, pp. 175–189. Oxford Univ. Press.
- YIP, W. H., WANG, R.-J. & MAK, T. C. W. (1990). *Acta Cryst.* **C46**, 717–719.

Acta Cryst. (1992). **C48**, 1214–1216

Structure of Dithiocyanato[(-)-spartein]cobalt(II)

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(Received 8 October 1991; accepted 4 December 1991)

Abstract. (Dodecahydro-7,14-methano-2*H*,6*H*-diprido[1,2-*a*:1',2'-*e*][1,5]diazocine-*N,N*)dithiocyanatocobalt(II), [Co(C₁₅H₂₆N₂)(NCS)₂], *M_r* = 409.5, orthorhombic, *P*2₁2₁2₁, *a* = 8.014 (4), *b* = 13.660 (7), *c* = 18.023 (7) Å, *V* = 1973.0 (16) Å³, *Z* = 4, *D_x* = 1.378 Mg m⁻³, λ(Mo *K*α) = 0.71069 Å, μ = 1.077 mm⁻¹, *F*(000) = 860, *T* = 290 K, *R* = 0.067 for 1208 observed reflections [*F* > 4.0σ(*F_o*)] and 169 parameters. A clear indication of absolute configuration [*η* = 1.13 (16)] is also obtained. The structure is found to be very similar to that of the dichloro[(-)-spartein]cobalt(II) complex characterized by Kuroda & Mason [*J. Chem. Soc. Dalton Trans.* (1977), pp. 371–373].

Introduction. As part of a study of *d*-electron optical activity, Mason & Peacock (1973) prepared a series of compounds of the type [*M*(spartein)*X*₂], where *M* = Co^{II}, Ni^{II}, Cu^{II} and Zn^{II}; and *X* = Cl⁻, Br⁻ or I⁻. Both magnetic moments and electronic spectra for the compounds were reported, as well as the differential absorption [or circular dichroism (CD)] of [Ni(sp)Cl₂]. Later, detailed studies of the *d*-electron optical activity of both dichloro[(-)-spartein]cobalt(II) (Drake, Kuroda, Mason, Peacock & Stewart, 1981) and dichloro[(-)-α-isosparteine]cobalt(II)

(Drake, Hirst, Kuroda & Mason, 1982) were reported.

A recent ligand-field study (Fenton & Gerloch, 1990) has successfully reproduced the *d-d* transition energies, intensities and differential absorption of these two Co compounds, as well as those of a third compound, dichloro[(+)-*N,N,N',N'*-tetramethyl-1,2-propylenediamine]cobalt(II). The authors found that they could reproduce both transition and differential absorption intensities only by inclusion of misdirected valency, or 'bent bonding', in the first coordination shell. The parameter set of the bent bonding was shown to correlate strongly with the detailed coordination geometry of the central metal ion. The two spartein complexes analysed possess pseudo-*C*₂ symmetry at the chromophore (Kuroda & Mason, 1977, 1979): the coordination planes CoNN' and CoClCl' are rotated from orthogonality by *ca* 6 and 19° in the two complexes following intramolecular steric crowding. The angle of rotation is important in determining part of the bent bonding in these complexes.

As part of a program to extend the ligand-field analysis to magneto circular dichroism (MCD) as well as natural CD, and to enlarge the range of object systems, we report here an X-ray structural

analysis of one further analogue of these molecules, viz. Co(sp)(NCS)₂.

Experimental. Dark-blue plate crystals were obtained by vapour diffusion from chloroform/ether. Crystal 0.10 × 0.15 × 0.58 mm; Siemens R3m/V diffractometer; graphite-monochromated Mo K α radiation; unit-cell parameters refined from 25 centred reflections ($15 < 2\theta < 25^\circ$); $\omega/2\theta$ scan mode, rate 2.00–14.65° min⁻¹ in ω , range 1.60° + K α separation; 2450 reflections measured, $5 < 2\theta < 42^\circ$ (*hkl* range: *h* 0–8, *k* 0–13, *l* –18–18); no significant variations for three standard reflections measured every 97 reflections; semi-empirical absorption correction applied with transmission ratios from 0.2428 to 0.3239; 2067 unique reflections ($R_{\text{int}} = 0.0087$); 1208 reflections with $F > 4\sigma(F)$. Structure solved by direct methods with full-matrix least-squares refinement on F^2 , minimizing $\sum w(F_o - F_c)^2$; anisotropic thermal parameters for the Co, the atoms of the thiocyanate ligand, and the five C atoms at the centre of the spartein ligand; H atoms fixed by riding with fixed isotropic thermal parameters; scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV); 169 parameters; $R = 0.067$, $wR = 0.076$, $w = [\sigma^2(F) + 0.0020F_o^2]^{-1}$; goodness of fit = 1.18; mean $\Delta/\sigma = 0.001$, maximum = 0.002; data:parameter ratio 7.1:1; largest peak in final difference map 0.95 e Å⁻³, largest hole –0.58 e Å⁻³. As our major interest in this system lies in its optical chirality, it seemed worthwhile to establish the absolute configuration of the molecule by refining the η parameter (Rogers, 1981), which is found to be 1.13 (16). The program *SHELXTL-Plus* (Sheldrick, 1987) was used throughout.

Discussion. Final atomic coordinates and equivalent isotropic temperature factors are listed in Table 1* and derived bond lengths and angles in Table 2.

A thermal ellipsoid plot with atom-numbering scheme is shown in Fig. 1. The coordination of the ligand atoms to the cobalt(II) ion is substantially distorted from tetrahedral, as in the structures of dichloro[(-)- α -isospartein]cobalt(II) (Kuroda & Mason, 1979) and dichloro[(-)-spartein]cobalt(II) (Kuroda & Mason, 1977). The central [CoN₂N'₂] chromophore is reduced to pseudo-C₂ symmetry, with an angle of 85.4° between the N(1), Co, N(2) and N(3), Co, N(4) planes. The angles between the N atoms of the spartein rings and the N atoms of the

Table 1. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($\text{\AA}^2 \times 10^3$)

Equivalent isotropic U is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
Co(1)	8492 (2)	7510 (2)	8127 (1)	52 (1)
N(1)	7332 (22)	8666 (12)	8505 (8)	72 (7)
C(1)	6655 (24)	9276 (15)	8808 (12)	69 (9)
S(1)	5763 (7)	10122 (4)	9258 (4)	93 (3)
N(2)	7072 (19)	6375 (13)	8282 (9)	82 (8)
C(2)	6319 (22)	5723 (13)	8513 (9)	49 (7)
S(2)	5216 (7)	4834 (4)	8792 (3)	87 (2)
N(3)	10887 (16)	7182 (8)	8423 (6)	52 (5)
C(3)	12092 (21)	7969 (12)	8228 (9)	57 (5)
C(4)	11646 (23)	8853 (12)	8677 (10)	76 (5)
C(5)	11746 (23)	8697 (14)	9475 (10)	84 (6)
C(6)	10656 (20)	7830 (12)	9715 (10)	76 (6)
C(7)	11003 (25)	6933 (13)	9251 (10)	82 (6)
N(4)	9237 (15)	7663 (11)	7046 (6)	56 (5)
C(8)	7692 (25)	7924 (15)	6648 (10)	96 (7)
C(9)	7802 (24)	7889 (13)	5812 (10)	83 (6)
C(10)	8321 (24)	6899 (14)	5550 (11)	84 (6)
C(11)	9929 (21)	6646 (14)	5924 (10)	72 (5)
C(12)	9763 (22)	6673 (13)	6767 (9)	63 (6)
C(13)	11444 (23)	6420 (15)	7172 (9)	65 (7)
C(14)	11286 (20)	6256 (12)	8018 (9)	64 (7)
C(15)	10545 (24)	8434 (12)	7027 (10)	67 (9)
C(16)	12166 (25)	8099 (15)	7407 (10)	65 (8)
C(17)	12783 (23)	7149 (17)	7047 (10)	99 (11)

Table 2. Bond lengths (\AA) and angles ($^\circ$)

Co(1)—N(1)	1.955 (16)	Co(1)—N(2)	1.944 (17)
Co(1)—N(3)	2.042 (13)	Co(1)—N(4)	2.049 (12)
N(1)—C(1)	1.134 (26)	C(1)—S(1)	1.584 (21)
N(2)—C(2)	1.153 (25)	C(2)—S(2)	1.584 (19)
N(3)—C(3)	1.487 (20)	N(3)—C(7)	1.534 (20)
N(3)—C(14)	1.494 (20)	C(3)—C(4)	1.496 (24)
C(3)—C(16)	1.493 (24)	C(4)—C(5)	1.456 (25)
C(5)—C(6)	1.533 (25)	C(6)—C(7)	1.510 (24)
N(4)—C(8)	1.475 (23)	N(4)—C(12)	1.501 (23)
N(4)—C(15)	1.487 (22)	C(8)—C(9)	1.510 (26)
C(9)—C(10)	1.491 (26)	C(10)—C(11)	1.495 (25)
C(11)—C(12)	1.526 (24)	C(12)—C(13)	1.571 (25)
C(13)—C(14)	1.546 (24)	C(13)—C(17)	1.481 (28)
C(15)—C(16)	1.538 (27)	C(16)—C(17)	1.532 (30)
N(1)—Co(1)—N(2)	108.4 (7)	N(1)—Co(1)—N(3)	122.2 (6)
N(2)—Co(1)—N(3)	109.7 (6)	N(1)—Co(1)—N(4)	112.9 (6)
N(2)—Co(1)—N(4)	112.9 (6)	N(3)—Co(1)—N(4)	89.8 (5)
Co(1)—N(1)—C(1)	171.4 (16)	N(1)—C(1)—S(1)	177.6 (21)
Co(1)—N(2)—C(2)	166.9 (15)	N(2)—C(2)—S(2)	176.8 (15)
Co(1)—N(3)—C(3)	113.0 (9)	Co(1)—N(3)—C(7)	111.1 (10)
C(3)—N(3)—C(7)	110.5 (12)	Co(1)—N(3)—C(14)	105.0 (9)
C(3)—N(3)—C(14)	111.0 (12)	C(7)—N(3)—C(14)	105.9 (11)
N(3)—C(3)—C(4)	107.5 (13)	N(3)—C(3)—C(16)	110.2 (14)
C(4)—C(3)—C(16)	116.7 (15)	C(3)—C(4)—C(5)	113.7 (15)
C(4)—C(3)—C(6)	111.1 (15)	C(5)—C(4)—C(7)	111.5 (14)
N(3)—C(7)—C(6)	110.3 (13)	Co(1)—N(4)—C(8)	104.0 (10)
Co(1)—N(4)—C(12)	107.9 (10)	C(8)—N(4)—C(12)	106.9 (13)
Co(1)—N(4)—C(15)	107.4 (10)	C(8)—N(4)—C(15)	114.2 (14)
C(12)—N(4)—C(15)	115.6 (12)	N(4)—C(8)—C(9)	115.4 (15)
C(8)—C(9)—C(10)	111.1 (15)	C(9)—C(10)—C(11)	107.9 (16)
C(10)—C(11)—C(12)	111.6 (14)	N(4)—C(12)—C(11)	112.3 (14)
N(4)—C(12)—C(13)	106.5 (13)	C(11)—C(12)—C(13)	112.5 (14)
C(12)—C(13)—C(14)	114.8 (14)	C(12)—C(13)—C(17)	113.8 (16)
C(14)—C(13)—C(17)	107.8 (14)	N(3)—C(14)—C(13)	112.1 (13)
N(4)—C(15)—C(16)	112.0 (14)	C(3)—C(16)—C(15)	116.3 (16)
C(3)—C(16)—C(17)	109.3 (16)	C(15)—C(16)—C(17)	109.7 (15)
C(13)—C(17)—C(16)	105.8 (15)		

thiocyanates differ [N(3)—Co—N(1) 122.2 (6) and N(4)—Co—N(2) 112.9 (6)°]; this again is similar to the effect seen in the dichloro complex.

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54931 (11 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HA0093]

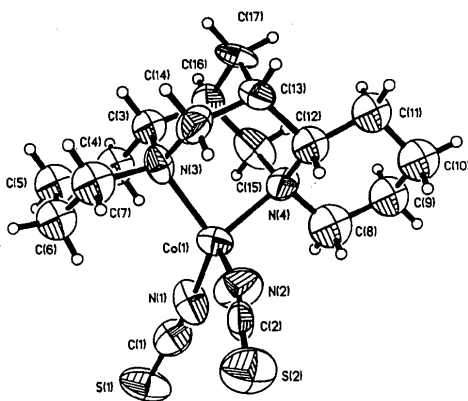


Fig. 1. Molecular structure of [Co{(-)-spartein}(NCS)₂] with 50% probability thermal ellipsoids for those atoms for which anisotropic vibration parameters were refined.

We thank Dr Alex Drake for providing the crystals used in this structure determination. KMJ thanks Downing College for a Bye-Fellowship, the

SERC and ICI for financial support, and Dr Malcolm Gerloch for his patience.

References

- DRAKE, A. F., HIRST, S. J., KURODA, R. & MASON, S. F. (1982). *Inorg. Chem.* **21**, 533–538.
- DRAKE, A. F., KURODA, R., MASON, S. F., PEACOCK, R. D. & STEWART, B. (1981). *J. Chem. Soc. Dalton Trans.* pp. 976–980.
- FENTON, N. D. & GERLOCH, M. (1990). *Inorg. Chem.* **29**, 3718–3726.
- KURODA, R. & MASON, S. F. (1977). *J. Chem. Soc. Dalton Trans.* pp. 371–373.
- KURODA, R. & MASON, S. F. (1979). *J. Chem. Soc. Dalton Trans.* pp. 727–730.
- MASON, S. F. & PEACOCK, R. D. (1973). *J. Chem. Soc. Dalton Trans.* pp. 226–228.
- ROGERS, D. (1981). *Acta Cryst.* **A37**, 734–741.
- SHELDRIK, G. M. (1987). *SHELXTL-Plus*. Release 3.4 for Nicolet R3m/V crystallographic system. Nicolet Instrument Corporation, Madison, Wisconsin, USA.

Acta Cryst. (1992). **C48**, 1216–1218

Structure of Bis(methylenedithio)tetrathiafulvalene Dicyanoargentate(I)

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(Received 14 May 1991; accepted 2 December 1991)

Abstract. [C₈H₄S₈][Ag(CN)₂], *M_r* = 516.54, orthorhombic, *Pmnm*, *a* = 8.794 (3), *b* = 20.333 (7), *c* = 4.247 (2) Å, *V* = 759.27 (4) Å³, *Z* = 2, *D_x* = 2.261 g cm⁻³, λ(Mo *Kα*) = 0.71069 Å, *F*(000) = 506, μ(Mo *Kα*) = 23.63 cm⁻¹, 614 observed room-temperature reflections, *R* = 0.023. The charge-transfer salt consists of C₈H₄S₈ cations (hereafter MT) and ribbons of infinite [Ag(CN)₂] anions with both the MT molecule and the Ag atoms on inversion centers. Ribbon distances are 2.103 (5) Å Ag—C, 3.305 (5) Å Ag—N, and 1.021 (7) Å C—N bonds; MT intramolecular distances are 1.407 (8) and 1.354 (5) Å C=C, 1.723 (3), 1.728 (2), 1.745 (3) and 1.816 (2) Å C—S and 2.942 (1), 2.972 (1), 3.075 (1) and 3.220 (1) Å S—S separations, typical of expected values for singly charged ions; near-neighbor contacts between ions involve 3.340 (1) Å Ag—S and 3.649 (1) to 3.678 (1) Å S—S separations.

Introduction. Various charge-transfer salts derived from bis(alkyldithio)tetrathiafulvalene have been shown to attain metallic and superconducting states at low temperature (Williams, Beno, Wang, Leung,

Enge, Geiser & Carlson, 1985). This is believed to result from the interstack interactions between the organic salt ions and has motivated the preparation of various salts to characterize better the structural properties responsible for such conductivity. Because of the highly symmetrical structure of MT, such interstack interactions might be strongly affected. This note reports on the structural details of MT·Ag(CN)₂.

Experimental. Single crystals of MT·Ag(CN)₂ were obtained by electrochemical oxidation at a platinum electrode in a 1 mM [N(C₄H₉)₄][Ag(CN)₂] solution with that of a corresponding dilute solution (1.3 mM) of MT in chlorobenzene using a current density of 0.4 A cm⁻². Only the single form crystallized in contrast to the observed various forms and hydrates found for the ethylene analog of bis(methylenedithio)tetrathiafulvalene (Kurmoo, Pritchard, Talham, Day, Stringer & Howard, 1990).

Tiny black needle-shaped crystals were obtained which proved to be of orthorhombic symmetry using precession photography. Systematic absences for