Square-planar Complexes of Pentane-2,4-dithione (Dithioacetylacetone): Crystal Structures of the Cobalt(II) and Nickel(II) Derivatives

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The crystal and molecular structure of the cobalt(II) and nickel(II) derivatives of dithioacetylacetone (sacsacH) have been determined by *X*-ray diffraction methods. Both crystals, being isomorphous, are orthorhombic, with space group *Cmca* and $Z = 4$. For Co(sacsac)$_2$: $a = 15{\cdot}64(2)$, $b = 14{\cdot}35(2)$, and $c = 6{\cdot}05(1)$ Å; for Ni(sacsac)$_2$: $a = 15{\cdot}592(6)$, $b = 14{\cdot}348(8)$, and $c = 5{\cdot}950(3)$ Å. The cobalt(II) structure was solved by conventional Patterson and Fourier methods and was refined by a least-squares method to R 0·11 for 437 independent reflections derived by photographic methods. For the nickel structure, 585 independent reflections, collected by counter methods, were used and the structure refined, by least squares, to R 0·044. The crystals are molecular with discrete monomeric molecular units of composition M(sacsac)$_2$. Each metal atom, located a site of symmetry $2/m$, is precisely coplanar with the four sulphur atoms bonded to it and, with an S–M–S intraligand bond angle of *ca.* 97°, the metal environment is conveniently described as square planar. However, the molecule as a whole is not planar being folded so that the dihedral angle between the MS$_4$ and the ligand planes is *ca.* 6°. The metal–sulphur bond distance is *ca.* 2·17 Å.

THE bivalent metal complexes of acetylacetone (pentane-2,4-dione, as acacH) and other related 1,3-diketones have been studied extensively because of their remarkable ability to form polymeric species in the solid state and in solutions of non-co-ordinating solvents. For example, the anhydrous nickel(II)[1] and cobalt(II)[2] derivatives of acacH are trimeric and tetrameric respectively with the metal atoms achieving an octahedral co-ordination in each case. Recently Martin and Stewart[3] reported the synthesis of a number of bivalent metal derivatives of the dithio-analogue of acacH, dithioacetylacetone (pentane-2,4-dithione, sacsacH). For the complexes (Co-(sacsac)$_2$ and Ni(sacsac)$_2$ the evidence, derived from a variety of physical measurements, suggested both to be simple monomeric square-planar complexes. This has been confirmed by single-crystal structure determinations, by use of *X*-ray diffraction methods, for each of the isomorphous pair Co(sacsac)$_2$ and Ni(sacsac)$_2$. A preliminary account of one of these structures has been published:[4] we report here a detailed account of both crystal structures.

EXPERIMENTAL

Data Collection.—(i) Co(sacsac)$_2$. Black needle crystals separated from a saturated solution in hot benzene.

The observed systematic absences were consistent with either space groups *Cmca* or *C2cb*;[5] a satisfactory solution was obtained for *Cmca*. Cell dimensions were obtained from Weissenberg photographs, taken about all three axes, calibrated by sodium chloride powder lines. Intensity data were estimated visually for the layers 0—6*kl* and *hk*0—4, approximate crystal dimensions being 0·1 × 0·1 × 0·15 mm for each case. Structure amplitudes for 437 observed independent reflections were corrected for Lorentz and polarization factors, but not for absorption or extinction effects.

(ii) Ni(sacsac)$_2$. Suitable crystals were obtained similarly and shown to be isomorphous with those of Co-(sacsac)$_2$. The data for refinement were obtained by use of a Siemens automatic single-crystal diffractometer, the crystal, of dimensions 0·06 × 0·08 × 0·50 mm, being mounted with its long direction coincident with the diffractometer ϕ axis. Accurate cell dimensions were obtained from the θ values determined for 12 strong and well-resolved high-angle reflections, the cell parameters being refined by a least-squares procedure.[6] Intensity measurements were made, by a ' five-values ' θ—2θ scan method,[7] to a Bragg angle of 70° with Cu-K_α Ni-filtered radiation, this gave, on the basis of the 3σ criterion, 585 independent statistically significant reflections. Structure amplitudes were corrected for Lorentz and polarization factors, and absorption effects,[8] but not for extinction.

Crystal Data.—(i) Co(sacsac)$_3$: $C_{10}H_{14}CoS_4$, $M = 321{\cdot}4$, Orthorhombic, $a = 15{\cdot}64(2)$, $b = 14{\cdot}35(2)$, $c = 6{\cdot}05(1)$ Å, $U = 1358$ Å^3, $D_m = 1{\cdot}57$, $Z = 4$, $D_c = 1{\cdot}57$ g cm^{-3}. Space group *Cmca* (D_{2h}^{18}, No, 64). Cobalt unfiltered radiation, $\lambda = 1{\cdot}7902$ Å, μ(Co-K_α) = 107·2 cm^{-1}. Single-crystal oscillation and Weissenberg photographs.

(ii) Ni(sacsac)$_2$. $C_{10}H_{14}NiS_4$, $M = 321{\cdot}2$, Orthorhombic, $a = 15{\cdot}592(6)$, $b = 14{\cdot}348(8)$, $c = 5{\cdot}950(3)$ Å, $U = 1331$ Å^3, $D_m = 1{\cdot}60$, $Z = 4$, $D_c = 1{\cdot}60$ g cm^{-3}. Space group *Cmca* (D_{2h}^{18}, No. 64). Cu-K_α radiation, $\lambda = 1{\cdot}5418$ Å; μ(Cu-K_α) = 73·2 cm^{-1}. Single-crystal oscillation and Weissenberg photographs, Siemens automatic diffractometer.

Structure Determination.—(i) Co(sacsac)$_2$. The cobalt atoms were assigned to special positions of the type (0,0,0; *etc.*) and the co-ordinates for the sulphur atom determined from the Patterson map. These positions were used to phase a three-dimensional electron-density distribution from which the remaining non-hydrogen atoms were located.

Refinement was achieved by the method of least squares, the function minimized being $\Sigma w\Delta^2$, where Δ is $\Sigma w(|F_o| - |F_c|)^2$, and w is the weight applied to each reflection by use of the weighting scheme: $w = F^*/|F_o|$ for $|F_c| > F^*$ and $w = |F_o|/F^*$ for $|F_o| < F^*$, F^* being taken as four times

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[1] J. C. Bullen, R. Mason, and P. Pauling, *Inorg. Chem.*, 1965, **4**, 456.

[2] F. A. Cotton and R. C. Elder, *Inorg. Chem.*, 1965, **4**, 1145.

[3] R. L. Martin and I. M. Stewart, *Nature*, 1966, **210**, 522.

[4] R. Beckett and B. F. Hoskins, *Chem. Comm.*, 1967, 909.

[5] ' International Tables for *X*-Ray Crystallography,' vol. I, Kynoch Press, Birmingham, 1952.

[6] W. R. Busing, R. D. Ellison, H. A. Levy, S. P. King, and R. T. Roseberry, Oak Ridge National Laboratory, Report ORNL 4143, 1968.

[7] W. Hoppe, *Angew. Chem. Internat. Edn.*, 1965, **6**, 508; Automatic Single-Crystal Diffractometer AED According to W. Hoppe,' users manual for Siemens Automated Diffractometer.

[8] G. W. Cox, personal communication; W. R. Busing and H. A. Levy, *Acta Cryst.*, 1957, **10**, 180.

the minimum observable structure amplitude, *i.e.* $F^* = 3{\cdot}2$. In the final stages of the refinement individual anisotropic temperature factors were assigned to the atoms and the refinement was continued until $\Sigma\Delta w^2$ was constant and the largest change in any parameter was $< 0{\cdot}01\sigma$. At this stage R was 0·11 and the weighted residual R' was 0·15.

Final atomic co-ordinates and temperature factor parameters, together with their estimated standard deviations, are given in Table 1.

(ii) Ni(sacsac)$_2$. The co-ordinates and individual isotropic temperature factors determined during the course of the refinement of Co(sacsac)$_2$ were used as a starting point in the refinement. Data were weighted according to the scheme described by Killean *et al.*,[9] so that each reflection was assigned a weight (w) according to the scheme:

$$w = [\sigma_{cs}^2 + A|F_o|^2 + B\sum_{i=1}^{m} f_i^2]^{-1},$$ where $A = 0{\cdot}005$ and $B = 0{\cdot}0001$. Anisotropic temperature factors were introduced and the refinement continued until there were no further changes in any of the parameters, when R was 0·044 and R' 0·076. The only hydrogen atom position indicated in a difference map was that bonded to C(2), and this was included in the final structure-factor calculations. Refinement terminated at R 0·044 and R' 0·067.

TABLE 1

Final atomic co-ordinates and thermal parameters * (Å^2 × 10^4), with estimated standard deviations in parentheses

(*a*) Ni(sacsac)$_2$

Atom	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ni	0·00000(0)	0·00000(0)	0·00000(0)	292(6)	307(6)	329(6)	0	0	−22(3)
S	0·10373(4)	0·06593(5)	0·17934(13)	353(6)	495(6)	432(6)	−66(2)	−15(2)	−102(3)
C(1)	0·07984(20)	0·12748(17)	0·41233(48)	456(16)	366(13)	380(15)	−66(10)	−37(12)	36(10)
C(2)	0·00000(0)	0·14949(36)	0·49777(68)	455(20)	457(18)	433(20)	0	0	0
C(3)	0·15722(25)	0·16168(28)	0·53786(59)	500(19)	656(20)	412(17)	−153(15)	−73(14)	−86(15)
H	0·00000	0·1960	0·6529	1544	1612	1006	0	0	−616

(*b*) Co(sacsac)$_2$

Atom	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Co	0·0000(0)	0·0000(0)	0·0000(0)	184(20)	234(18)	350(22)	0	0	−15(13)
S	0·1036(2)	0·0630(2)	0·1846(5)	233(16)	361(17)	571(21)	81(11)	−4(12)	−109(12)
C(1)	0·0795(8)	0·1287(8)	0·4132(20)	445(73)	337(63)	360(62)	26(51)	−53(58)	55(49)
C(2)	0·0000(0)	0·1534(28)	0·4913(9)	440(114)	268(85)	498(107)	0	0	−105(72)
C(3)	0·1583(10)	0·1626(11)	0·5367(23)	477(86)	752(100)	482(76)	−286(78)	−87(66)	−76(70)

* The temperature factor expression is $T = \exp[-2\pi^2(U_{11}h^2a^{*2} + 2U_{12}hka^*b^* + etc.)]$

Final atomic co-ordinates and thermal parameters, together with their estimated standard deviation, are also in Table 1.

Scattering factors for Ni^{2+}, Co^{2+}, C, and S were taken from ref. 10, with the nickel, cobalt, and sulphur values corrected for anomalous dispersion.[11] Observed and calculated structure factors, for both compounds, are listed in Supplementary Publication No. SUP 20921 (7 pp., 1 microfiche).[*]

RESULTS AND DISCUSSION [†]

Crystals of Ni(sacsac)$_2$ and Co(sacsac)$_2$ are both composed of discrete neutral molecules held together by van der Waals forces. The molecules are approximately planar and arranged so that the plane of the molecules is parallel to the b axis of the crystal. The packing of the molecules in the unit cell is shown in projections in Figures 1 and 2. There are no abnormally short contacts, all distances being compatible with the accepted values for non-bonded interactions between various groups,[12] the shortest of the non-hydrogen contacts for the nickel structure being 3·68 Å between the nickel atom of one molecule, of centre (0,0,0) and two carbon atoms [both C(2)] of molecules with centres (0,0,±1).

The molecular structure of Ni(sacsac)$_2$ is shown in Figure 1 which also gives the atomic labelling and the bond lengths and angles, together with their estimated standard deviations are given in Tables 2 and 3. The

TABLE 2

Comparison of interatomic distances (Å) in Ni(sacsac)$_2$ and Co(sacsac)$_2$

Bond	Ni(sacsac)$_2$	Co(sacsac)$_2$
M–S	2·156(1)	2·166(3)
S–C(1)	1·685(3)	1·716(13)
C(1)–C(2)	1·381(4)	1·376(15)
C(1)–C(3)	1·510(5)	1·521(19)
C(2)–H	1·14	
S · · · S(1)	3·235(2)	3·242(6)
S · · · S(2)	2·852(2)	2·874(6)

TABLE 3

Comparison of the bond angles (deg.) in Ni(sacsac)$_2$ and Co(sacsac)$_2$

Angle	Ni(sacsac)$_2$	Co(sacsac)$_2$
S–M–S(1)	97·20(4)	96·9(2)
S–M–S(2)	82·80(4)	83·1(2)
M–S–C(1)	118·1(1)	118·7(5)
S–C(1)–C(2)	128·4(3)	128·1(11)
S–C(1)–C(3)	113·8(3)	113·2(10)
C(1)–C(2)–C(11)	128·7(4)	129·2(16)
C(2)–C(1)–C(3)	117·8(3)	118·7(12)
C(1)–C(2)–H	115·6	

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[*] See Notice to Authors No. 7 in *J.C.S. Dalton*, 1972, Index issue.

[†] Except for the details of the cobalt environment in Co(sacsac)$_2$ the subsequent discussion will be restricted to the dimensions of the more accurately determined nickel complex.

[9] R. C. G. Killean, *Acta Cryst.*, 1967, **23**, 54; R. C. G. Killean, *Acta Cryst.*, 1967, **23**, 1109; D. F. Grant, R. C. G. Killean, and J. L. Lawerence, *ibid.*, 1969, *B*, **25**, 374.

[10] Ref. 5, vol. III, 1962, p. 201, *et seq.*

[11] Ref. 10, p. 214.

[12] L. Pauling, 'The Nature of the Chemical Bond,' 3rd edn., Cornell University Press, 1960, p. 260; A. Bondi, *J. Phys. Chem.*, 1964, **68**, 441.

molecule is not precisely planar, being folded, or ' hinged ', about two lines, one passing through S and S(1) and the other through S(2) and S(3), to give a stepped structure (Figure 2). The dihedral angle between the NiS_4 plane and the plane of best fit through the ligand atoms is 8·6°, the nickel atom being 0·209 Å out of the plane of the ligand.

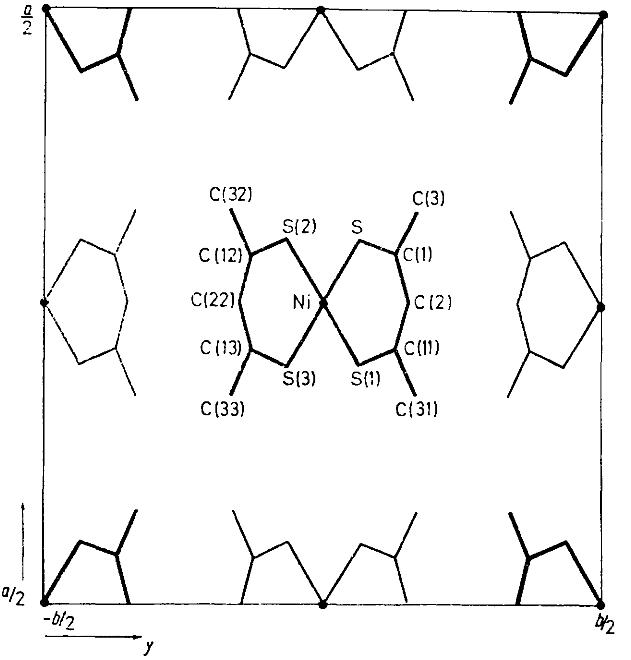

FIGURE 1 Projection of the crystal structure of $Ni(sacsac)_2$ on the (001) plane. The labelling of the atoms is given for the molecules at (0,0,0)

The Metal Environment.—Each nickel atom is covalently bonded to four sulphur atoms and since each metal atom is situated on a site of symmetry $2/m$, all five atoms are required to be exactly coplanar. Since the angle subtended at the nickel atom by sulphur atoms of the same ligand is 97·20(4)°, which is not too different from 90°, the nickel stereochemistry is conveniently described as distorted square planar.

The Ni–S bond length of 2·156(1) Å is within the range of previously reported distances (2·15—2·16 Å) for square-planar nickel(II) complexes containing nickel to sulphur bonds.[13] However, it is considerably shorter than the Ni–S distances found for octahedral nickel(II) complexes which fall in the range 2·4—2·6 Å;[14] this effect also appears to occur in nickel(II) complexes involving first-row donor atoms.

In the cobalt complex, the metal atom has an environment identical to that of the nickel complex. Square-planar co-ordination is unusual for Co^{II}, only three examples having been substantiated: bis(tetra-n-butylammonium) bis(maleonitriledithiolato)cobaltate(II),[15] *trans*-dimesitylbis(diethylphenylphosphine)cobalt(II),[16] and cobalt(II) phthalocyanine.[17] The preferred geometries of cobalt(II) are tetrahedral and octahedral: polymeric species are often formed giving rise to the higher co-ordination number. However, a few low-spin bis complexes are known, these too, are presumably square planar.[18]

The cobalt–sulphur distance [2·166(3) Å] is considerably less than the value (*ca.* 2·3 Å) found for it in other stereochemistires.[19] However, this distance is in good agreement with the only other Co–S distance (2·16 Å), so far reported for a square-planar complex.[15] This short distance may be due to an increased amount of metal–sulphur π-bonding, favoured for the planar case; the electrostatic theory, based on d orbital population for different metal geometries,[14] and used to explain the short nickel–oxygen distance in bis(dipivaloylmethanido)-nickel(II), may also be relevant here.[20]

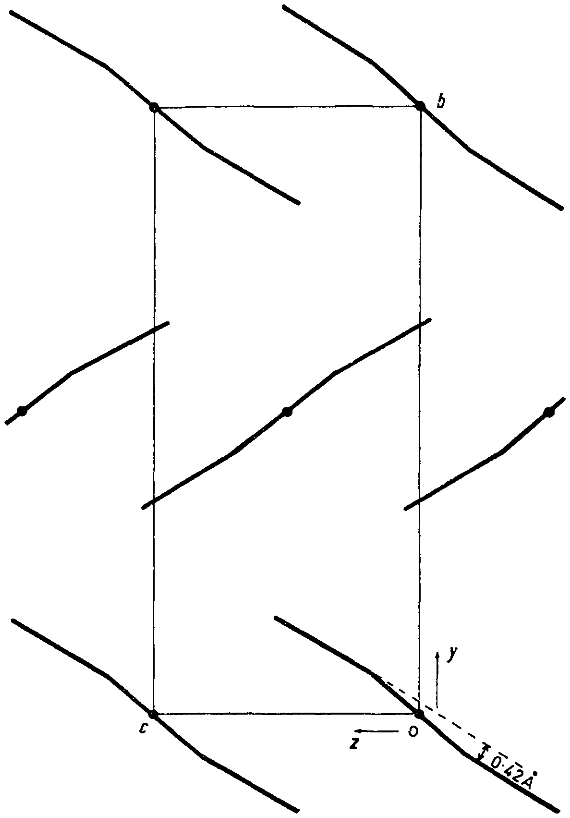

FIGURE 2 Projection of the crystal structure of $Ni(sacsac)_2$ on the (100) plane. The dotted lines on the molecule at (0,0,0) show the ' stepped ' structure

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[13] I. D. Brown, C. P. Weiss, and K. K. Wu, ' Bond Index to the Determinations of Inorganic Crystal Structures,' McMasters University, Hamilton, Ontario, 1969, 1970, and 1971; R. Beckett, Ph.D. Thesis, University of Melbourne, 1972, p. 60.

[14] A. Lopex-Casto and M. R. Truter, *J. Chem. Soc.*, 1963, 1309.

[15] J. D. Forrester, A. Salkin, and H. Templeton, *Inorg. Chem.*, 1964, **3**, 1500.

[16] P. G. Owston and J. M. Rowe, *J. Chem. Soc.*, 1963, 3411.

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[19] F. A. Cotton and D. L. Weaver, *J. Amer. Chem. Soc.*, 1965, **87**, 4189; S. Bruckner, M. Calligaris, G. Nardin, and L. Randaccio, *Chem. Comm.*, 1969, 474.

[20] F. A. Cotton and J. J. Wise, *Inorg. Chem.*, 1966, **5**, 1200.

The Ligand.—All attempts to isolate the free ligand dithioacetylacetone have been unsuccessful and all its metal derivatives have been prepared *in situ.* The structure determinations of $Ni(sacsac)_2$ and $Co(sacsac)_2$ confirm the existence of the ligand with the structure predicted.

The crystal symmetry requires that the ligand has two-fold symmetry, and hence that certain bond lengths and angles are equivalent. The C–S bond lengths [1·685(3) Å], are comparable to those observed for other compounds where extensive delocalization has been predicted. The C(1)–C(2) distance [1·381(4) Å] is almost identical to the value expected for an aromatic system, and the C(1)–C(3) distance [1·509(5) Å] is consistent with the usual values obtained for a single bond between sp^2 and sp^3 hybridized carbon atoms.[21]

The ligand moiety is perfectly planar, so that the condition for effective overlap of p orbitals and hence delocalization is satisfied, although the metal atom is not in this plane.

Two further features of the structure are: first, most of the internal bond angles in the chelate ring are larger than would be predicted by use of a simple hybridization scheme for each atom. This results in the external angles S–C(1)–C(3) and C(2)–C(1)–C(3) being depressed from their expected values, with the ligand ' bite ' being increased to the quite large value of 3·235(2) Å. Secondly, this opening of the intraligand S–Co–S angle causes the interligand S · · · S distance to be decreased to 2·852(2) Å, which is significantly less than twice the van der Waals radius given for sulphur ($2 \times 1{\cdot}76 = 3{\cdot}52$ Å),[12] which suggests that there is some interaction between these two atoms.

A possible explanation for the deviation of the bond angles from their expected values can be made in terms of simple geometrical considerations. For any planar six-membered ring structure the sum of the internal bond angles must total 720°. For a six-membered chelate ring, where the preferred valence angle of the metal atom is 90°, as in $Co(sacsac)_2$, the sum of the valency angles will be only 690°. Therefore, in order to maintain planarity some of the bond angles within the ring must adopt values greater than those normally associated with them. This effect is enhanced in $Co(sacsac)_2$ because of the much longer metal–sulphur (relative to carbon–carbon and carbon–sulphur) distances. This is in agreement with values obtained for all of internal angles of the chelate ring of $Ni(sacsac)_2$, except for Ni–S–C(1), the angular strain being relieved to some extent by the slight folding along the S · · · S(1) line. One possible reason for the exception is that the lone pairs on the sulphur atom exert a stronger stereochemical influence than do the bonding pairs of electrons attached to the carbon and metal atoms.[22]

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