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Bis(dithiobiureto)M^{II}, M=Pt, Pd

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Abstract. $(S_2C_2N_3H_4)_2M$, M=Pd or Pt, are isomorphous with identical cell parameters within experimental accuracy: orthorhombic, *Pbca*; $Z=4$; $a=8{\cdot}804$ (2), $b=12{\cdot}170$ (8), $c=10{\cdot}463$ (7) Å; $\varrho_o=\varrho_c=2{\cdot}28$ and 2·87 g cm^{-3}, respectively. The important structural features are a non-planar isolated $(S_2C_2N_3H_4)_2M$ moiety with four-coordinate planar MS_4 metal geometry and M–S distances of 2·29 Å.

Introduction. Dithiobiuret, $S_2C_2N_3H_5$, is an interesting ligand for transition metals: (1) It is closely related to the ligand MNT (maleonitriledithiolate) for which an extensive interesting redox chemistry has been developed (Schrauzer, 1969); (2) It has an abundance of non-bonding π electrons that may have important structural effects upon complexation (Girling & Amma, 1968; Lüth, Hall, Spofford & Amma, 1969); (3) It is closely related to the ligand biuret, yet appears to bind only *via* the S atom to metal whereas biuret binds through oxygens (Freeman, 1967) or O and N depending upon conditions; (4) In contrast to the reactions of biuret, this ligand readily loses a proton from the central N atom. We report here the structural details for the bis(dithiobiureto) Pd and Pt compounds which have significant structural differences from the analogous Ni compound (Lüth, Hall, Spofford & Amma, 1969; Pignedoli, Peyronel & Antolini, 1972). These differences will be discussed and correlated with the size and electronic structure of the metals elsewhere (Gash & Amma, 1976).

Yellow-orange crystals of the above compounds were grown by recrystallization of the crude reaction products from 2:1 ethanol–water mixtures. This crude reaction mixture was prepared by combining 25 ml of a saturated aqueous solution (80 °C) of dithiobiuret with a like volume of 0·04 *M* K_2PdCl_4 or K_2PtCl_4 and heating to 80 °C for approximately 15 min; the product and some by-product precipitated overnight.

Source: Mo $K\alpha$, $\lambda=0{\cdot}71068$ Å; $2\theta_{max}=66$, 62°; θ–2θ scan on a Picker automated diffractometer, $\Delta 2\theta=1{\cdot}4$, 1·2°. Number of reflections: 2122, 1463 taken; 833, 464 non-zero. Rejection level $3\times K(B_1+B_2)^{1/2}$ where K=scaling of background time to scan time and is 2·09 and 7·20; $\mu=22{\cdot}9$, 144 cm^{-1}, crystal size: $0{\cdot}12\times 0{\cdot}10\times 0{\cdot}64$ mm; $0{\cdot}21\times 0{\cdot}16\times 0{\cdot}70$ mm; R(final) = 0·046, 0·056; weighted $R=0{\cdot}038$, 0·067 respectively, for the Pd and Pt compounds.

Structure solution was by standard heavy-atom techniques and refinement was by full-matrix least-squares calculations. The function minimized was $\sum w(F_o-F_c)^2$ with weights determined from counting statistics. Scattering factors for Pd^{2+}, Pt^{2+} and neutral N and C were from Cromer & Waber (1965), those for H were from Stewart, Davidson & Simpson (1965). The effects of anomalous dispersion were included in the structure factor calculations by addition to F_c (Ibers & Hamilton, 1964). Values for $\Delta f'$ and $\Delta f''$ for Pd, Pt and S were those given by Cromer (1965).

All non-hydrogen thermal parameters were varied anisotropically, but hydrogen parameters were varied

Table 1. $Pd(S_2C_2N_3H_4)_2$: *final atomic positional and thermal parameters and estimated standard deviations*

Positional parameters for the analogous Pt compound are not significantly different from those above; of course, the thermal parameters do differ. Numbers in parentheses here and in succeeding tables are estimated standard deviations in the least significant digits. A fixed parameter is indicated by (−). Anisotropic temperature factors are of the form:

$$\exp\left[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)\times 10^{-4}\right].$$

	x	y	z	B or β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Pd	0·0000 (−)	0·0000 (−)	0·0000 (−)	81 (1)	32 (1)	48 (1)	1 (1)	−1 (1)	−1 (1)
S(1)	0·0183 (2)	−0·1321 (1)	0·1565 (1)	165 (3)	34 (1)	57 (1)	−6 (1)	−118 (2)	2 (1)
S(2)	0·1782 (2)	0·1093 (1)	0·0959 (1)	103 (2)	47 (1)	59 (1)	−17 (1)	1 (2)	2 (1)
C(1)	0·0309 (7)	−0·0686 (6)	0·3022 (6)	85 (11)	42 (4)	53 (5)	0 (5)	−7 (5)	4 (3)
C(2)	0·1777 (7)	0·0931 (5)	0·2615 (6)	58 (7)	36 (4)	58 (5)	−1 (4)	−17 (5)	0 (4)
N(1)	−0·0283 (10)	−0·1245 (6)	0·4003 (7)	176 (15)	61 (5)	62 (5)	−35 (7)	18 (8)	2 (4)
N(2)	0·2707 (8)	0·1622 (6)	0·3197 (7)	121 (10)	52 (5)	69 (5)	−18 (5)	−13 (7)	0 (4)
N(3)	0·0974 (7)	0·0266 (4)	0·3373 (6)	83 (7)	45 (4)	60 (5)	−5 (4)	−4 (5)	−1 (3)
H(1)	−0·0562 (129)	−0·1010 (98)	0·4638 (118)	5·8 (43)					
H(2)	−0·0983 (132)	−0·1799 (103)	0·3646 (100)	6·0 (71)					
H(3)	0·2686 (70)	0·1549 (54)	0·3954 (61)	0·6 (23)					
H(4)	0·3169 (128)	0·2093 (99)	0·2770 (109)	6·7 (53)					

only isotropically. A final difference electron density map was qualitatively featureless. Final atomic positional and thermal parameters are in Table 1.* Interatomic distances and angles and their errors were computed with the parameters and variance–covariance matrix from the last cycle of least squares and are shown in Fig. 1.

Discussion. The structure may be described as isolated molecular units of $(S_2C_2N_3H_4)_2M$, where M is Pt or Pd, with only van der Waals interactions between these units (Fig. 1). There is no evidence from interatomic distances of hydrogen bonding, of metal–metal interaction nor of any metal–adjacent ligand bonding (Fig. 2).

Table 2. *Torsion angles about bonds in the* PdS_2C_2N *ring*

Pd—S(1)	+41 (2)°	N(3)–C(2)	−23 (6)°
S(1)–C(1)	−35 (4)	C(2)–S(2)	−3 (4)
C(1)–N(3)	−3 (6)	S(2)–Pd	+30 (2)

The metal lies on a crystallographic center of symmetry and is bound to four S atoms from two different ligands in a planar MS_4 array. However, the entire molecule is not planar but distorted into a chair conformation as indicated by the torsion angles in Table 2. In addition, the S–M–S angles are not 90° but expanded to 92·65 (7)° within the chelate ring. The chelate S–S bite distance is also larger at 3·319 (2) Å than is the interligand S–S distance at 3·169 (2) Å. The M–S distance is only slightly shorter (0·04 Å) than that found in Pd, Pt complexes with thiourea (Berta, Spofford, Boldrini & Amma, 1970; Girling & Amma, 1968). It is interesting to note that even though the ligand is not planar in this complex, the individual $\left(S\text{–}C\begin{smallmatrix}N\\N\end{smallmatrix}\right)$ units are planar.

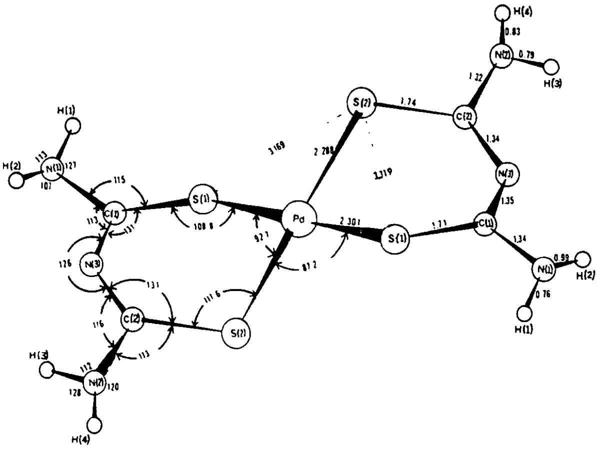

Fig. 1. A perspective view of the Pd(Pt) $(S_2C_2N_3H_4)_2$ molecule with relevant interatomic distances and angles. The metal site is a crystallographic center of symmetry, and therefore angles are on one half and distances on the other. The e.s.d.'s are: M–S ± 0·001, S–C ± 0·007, C–N ± 0·01, N–H ± 0·1, S–S ± 0·002 Å, or less; for interatomic angles the e.s.d.'s are: S–M–S ± 0·07, M–S–C ± 0·2, S–C–N ± 0·6, C–N–C ± 0·6, C–N–H ± 1·0, H–N–H ± 1·0°, or less.

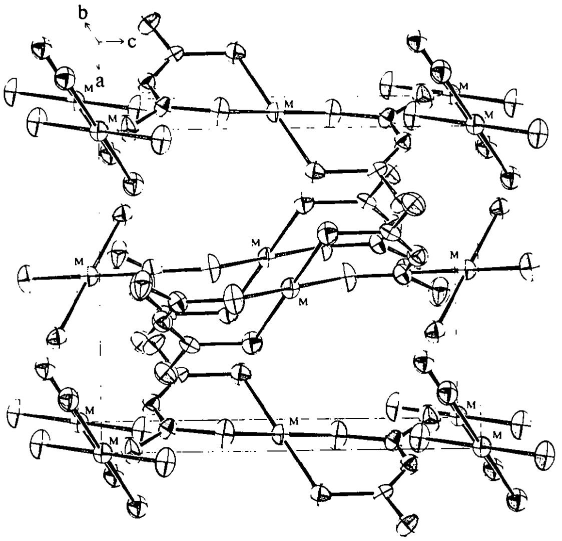

Fig. 2. An *ORTEP* view of the contents of the unit cell. The origin is in the upper left-hand front corner and a 4° rotation in each direction has been effected to show overlap. The metal atoms (M) at 0,0,0; $\frac{1}{2},\frac{1}{2}$,0 and their unit translation equivalents have only the S atoms bound to them shown for clarity. However, for the metal atoms at 0,$\frac{1}{2},\frac{1}{2}$; $\frac{1}{2}$,0,$\frac{1}{2}$ and their translation equivalents the entire molecule is shown. The thermal ellipsoids are shown at the 50% probability level.

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* A list of structure factors and a table of the final atomic positional and thermal parameters for M=Pt have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31865 (11 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

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