system where the isomerization above was interpreted as a change from $CoNH_2CH_2CN \rightarrow CoN{\equiv}CCH_2NH_2$ coordination with concomitant cis → trans rearrangement.

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Metal–Metal Bonding in Nickel Triad Complexes. The X-Ray Crystal Structure of a Platinum(II) Compound, $Pt_2(S_2CC_6H_4C_3H_7)_4$, Containing a Platinum–Platinum Bond

Sir:

Recently Baird[1] described metal–metal bonding in nickel triad complexes as "very rare." Using structural criteria as an indication of metal–metal bonding, this situation is changing rapidly,[2,3] although heretofore no discrete molecular species containing platinum(II) has been reported[4] with a metal–metal distance short enough (<3.0 Å) to conclude the existence of metal–metal bonding.

The detailed synthesis of $Pt_2(S_2CC_6H_4\text{-}i\text{-}Pr)_4$, *i*-Pr = $-CH(CH_3)_2$, will be reported elsewhere.[5] This compound appears to be representative of dithioaromatic acid complexes of platinum(II) but unlike those of nickel(II)[6] or palladium(II).[7]

Precession and Weissenberg photographs showed only $\bar{1}$ symmetry. Data (~5000 reflections) were collected on a Picker automatic diffractometer using nickel-filtered Cu Kα radiation. Standard techniques[8] were used to treat the data leaving 4225 independent (absorption corrected) reflections which satisfy observability criteria.[8]

After removing reflections $I/\sigma_I < 3.0$, final isotropic refinement for all 50 atoms in $P\bar{1}$ with real and imaginary anomalous scattering factors[9] produced $R = 0.125$. Introduction of a Cruickshank weighting scheme and anisotropic thermal parameters for Pt and S produced a converged R factor of 0.099 with a weighted R, $[\Sigma w \cdot (|F_o| - |F_c|)^2]^{1/2}/\Sigma|F_o|$, of 0.125. Since the platinum atoms strongly dominate the X-ray scattering and hence limit the reliability of the carbon atom positions, refinement was terminated.

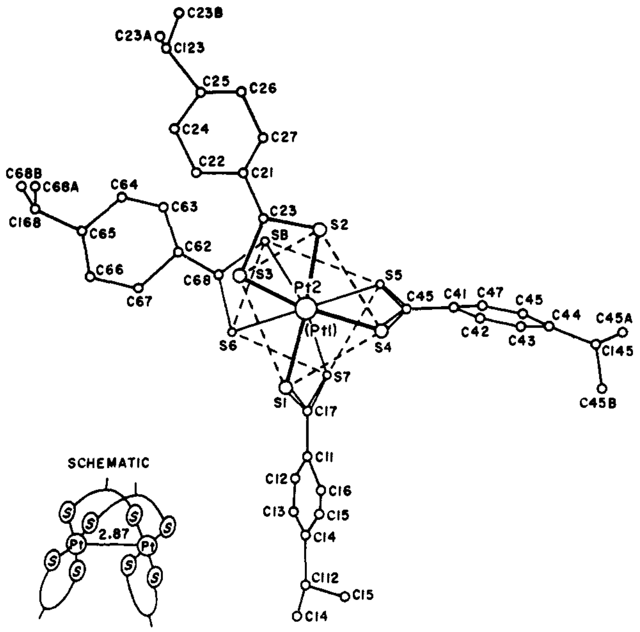

Figure 1. The molecular structure of $Pt_2(S_2CC_6H_4C_3H_7)_4$.

The structure of the dithiocumate complex (Figure 1) of platinum(II) can be described as an approximate square antiprism of sulfur atoms containing platinum(II) atoms in the two square faces. The angle between the two planes defined by the sulfur atoms coordinated to platinum(II) is 12.4° and the platinum atoms deviate from these planes toward each other by 0.05–0.10 Å. There are two bridging ligands and two terminal ligands, a structural feature easily recognized in the vibrational spectrum of the complex[10] and first suggested by nuclear magnetic resonance measurements. The bond lengths and angles (Table I) for the terminal dithiocumate ligands compare favorably with those reported by Swift[11] for $Pt(S_2CC_6H_4\text{-}i\text{-}Pr)_2P(C_6H_5)_3$. (This latter compound has essentially planar PtS_3P coordination with the dangling sulfur atom 3.58 Å from the platinum(II).)

The presence of both terminal and bridging 1,1-dithiolate ligands is reminiscent of the structure of $[Fe(S_2CSC_2H_5)_2(SC_2H_5)]_2$ reported by Coucouvanis, *et al.*,[12] in which there are both bridging and terminal thioxanthate ligands.

The metal–metal distance[13] reported for stacked (columnar) linear "polymers" such as $[Pt(NH_3)_4][PtCl_4]$, $[Pd(NH_3)_4][PtCl_4]$, Pd(dimethylglyoximate)$_2$, etc., appears to be ~3.25 Å with one known exception, namely partially oxidized $K_2[Pt(C_2O_4)_2]\cdot 2H_2O$, as reported by Krogmann[14] where the Pt–Pt distance is 2.85

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(1) M. C. Baird, *Progr. Inorg. Chem.*, **9**, 1 (1968).

(2) M. Bonamico, G. Dessy, and V. Fares, *Chem. Commun.*, 1106 (1969).

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(4) The compound $Pt_3[P(C_6H_5)_3]_3S(CO)$ contains a 2.647-Å Pt–Pt bond: A. C. Skapski and P. G. H. Troughton, *J. Chem. Soc. A*, 2772 (1969). The shortest recorded Pt–Pt distance in a molecular species appears in $(C_8H_{12})_3Pt_3(SnCl_3)_2$ [L. J. Guggenberger, *Chem. Commun.*, 512 (1968)] where it is 2.58 (1) Å. K. K. Chering, R. J. Cross, K. P. Forrest, R. Wardle, and M. Mercer, *ibid.*, 875 (1971), recently reported the structure of $Pt_2C_{20}H_{20}$, a complex of π-cyclopentadiene, containing a Pt–Pt distance of 2.581 Å. In each of these compounds, platinum is reduced below the oxidation state of two. The Pt–Pt distance in platinum metal is 2.77 Å.

(5) J. P. Fackler, Jr., J. A. Fetchin, and D. Fries, to be submitted for publication.

(6) M. Bonamico, G. Dessy, and V. Fares, *Chem. Commun.*, 324 (1969).

(7) M. Bonamico and G. Dessy, *ibid.*, 483 (1968).

(8) G. H. Stout and L. H. Jensen, "X-ray Structure Determination," Macmillan, New York, N. Y., 1968, p 454 ff; $\sigma_{I_{\text{rel}}} = [\sigma_{PK}^2 + (0.02N_{PK})^2]^{1/2}$.

(9) "International Tables for X-ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, 1962. Programs utilized were versions adopted for the Univac 1108; PICK 1, 2 the diffractometer setting and cell constant program due to K. Knox; Corr 3 data reduction (D. C. Rohrer); ABSCOR, the absorption program of B. Lee and V. Day as modified by K. Knox; GENFR, a Fourier program produced by S. T. Rao; a local version of the Busy-Martin-Levy structure factor calculation and least-squares refinement program (ORFLS) ORFEE; MASTER, a bond angle–bond length program written by S. T. Rao.

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Table I. Selected Bond Lengths (Å) and Bond Angles (Deg)

Bond	Distance	Bond	Distance
Pt(2)-Pt(1)	2.870 (3)	C(45)-S(4)	1.73 (5)
Pt(1)-S(5)	2.336 (7)	C(45)-S(5)	1.64 (4)
Pt(1)-S(6)	2.309 (7)	C(17)-S(1)	1.66 (6)
Pt(1)-S(7)	2.277 (10)	C(17)-S(7)	1.72 (5)
Pt(1)-S(8)	2.322 (8)	C(17)-C(11)	1.50 (6)
Pt(2)-S(1)	2.318 (10)	C(45)-C(41)	1.48 (4)
Pt(2)-S(2)	2.314 (10)	C(68)-C(62)	1.38 (4)
Pt(2)-S(3)	2.323 (7)	C(23)-C(21)	1.42 (6)
Pt(2)-S(4)	2.283 (6)		
C(23)-S(2)	1.69 (3)	Bonds	Angle
C(23)-S(3)	1.68 (4)	S(6)-Pt(1)-S(8)	73.9 (5)
C(68)-S(6)	1.71 (4)	S(5)-Pt(1)-S(8)	100.8 (4)
C(68)-S(8)	1.72 (4)	S(6)-Pt(1)-S(7)	92.8 (5)
		S(5)-Pt(1)-S(7)	92.0 (5)
Some Nonbonded distances		S(3)-Pt(2)-S(2)	73.2 (4)
S(4)-S(7)	3.48 (3)	S(3)-Pt(2)-S(1)	100.8 (5)
S(4)-S(5)	3.00 (3)	S(2)-Pt(2)-S(4)	96.5 (5)
S(2)-S(8)	3.73 (4)	S(1)-Pt(2)-S(4)	89.5 (5)
		S(4)-C(45)-S(5)	125.5 (26)
		S(6)-C(68)-S(8)	108.3 (23)

Angle between S(1)-S(2)-S(3)-S(4) and S(5)-S(6)-S(7)-S(8) planes, 12.4°

Rms deviation (Å) of platinum atoms from planes[a] Pt(1), +0.10 Pt(2), −0.05

[a] Standard deviation of atoms in plane <0.005 Å. Cell dimensions $a = 15.564$ (6), $b = 15.480$ (6), $c = 12.555$ (3) Å; $\alpha = 90.58$ (1)°, $\beta = 116.80$ (1)°, $\gamma = 122.55$ (1).

Å. In these "one-dimensional metal chain" compounds[15] Rundle[16] and others[17] have suggested the existence of metal–metal bonding formed by overlap of d_{z^2} and p_z orbitals on the metal atoms. This overlap[18] apparently leads to various anisotropic physical properties such as electron conduction along the metal–metal chain.[19]

σ overlap does not specify the relative rotational orientation of one metal–ligand plane with respect to another. Thus it appears significant that in compounds thought to contain a Pt(II)–Pt(II) bond, one idealized metal–ligand square is rotated from the next nearest ML_4 square toward a staggered L_4M–ML_4 structure. In no case is the M_2L_8 geometry close to the eclipsed structures of $Re_2Cl_8^{2-}$, $Cu_2(O_2CCH_3)_4 \cdot 2H_2O$, or several other species[20] some of which contain multiple metal–metal bonding.

Assuming a σ overlap between the metal atom centers, a staggered configuration minimizes the interaction between the filled nonbonding d_{xy} orbitals (in planar d^8 complexes) on adjacent metal atom centers. Alternatively, overlap of the filled nonbonding d_{xy} orbital on one center with the empty $d_{x^2-y^2}$ orbital on the next center is maximized when one ML_4 square is rotated 45° relative to the next one. This d–d orbital interaction leads to net δ bond formation. The very large S–C–S angle in the bridging dithiocumate ligands compared with the terminal ligands seems to exclude consideration of steric interactions between sulfur atoms as the primary cause of the antiprismatic structure.[21]

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(19) See ref 15 for a recent discussion of the bonding.

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(21) The support of the National Science Foundation, GP-11701, is gratefully acknowledged. This structure was reported in part at the 161st National Meeting of the American Chemical Society, Los Angeles, Calif., March 1971, Abstracts, INOR 129.

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Preparation and Solvolysis of Optically Active 1,2-Dimethyl-*exo*-2-norbornyl Chloride. Direct Evidence for a Classical Bicyclo[2.2.1]hept-2-yl Carbonium Ion[1]

Sir:

We wish to report that low-temperature hydrochlorination of optically active 1-methyl-2-methylenenorbornane (I) gives active 1,2-dimethyl-*exo*-2-norbornyl chloride (II-Cl) and methanolysis of the latter gives active products. Thus, neither hydrochlorination nor solvolysis passes through a symmetrical intermediate—in this system, as in the parent norbornyl system, the bridged nonclassical ion is symmetrical and the classical ion is asymmetric.

The report[2] that hydrochlorination of deuterium-labeled I does not result in randomization of the methyl groups in the product suggested that active II-Cl could be prepared from active I. Under conditions reported[2] to give minimum (35%) scrambling to the methyl groups (hydrochlorination of neat I at 0°) the reaction does not go to completion and we were unable to separate active chloride from the unreacted olefin.[3] However, optically active II-Cl was obtained in pure form as follows.

Hydrochlorination[2] of a precooled pentane solution of (−)-I[4] at −78° was complete in about 2 min. The reaction flask was immediately chilled with liquid nitrogen and attached to a vacuum line and the pentane and excess HCl were vacuum transferred as the reaction flask was warmed to 0°. Efficient stirring during hydrochlorination and rapid work-up are necessary to avoid extensive racemization. The residual (−)-II-Cl, mp 120–122° dec, was shown to be homogeneous by elemental analysis and solvolysis equivalent. The spectral properties were the same as those of racemic II-Cl and the mass spectrum had parent peaks at 158 and 160. Absence of unreacted (−)-I (which has a much higher rotation) was clear from the nmr spectrum and rotary dispersion curves for the two compounds. The chloride racemizes in chloroform ($k \sim 4 \times 10^{-3}$ min^{-1} at 30°) and accurate rotations could not be determined. The most active samples had $[\alpha]\text{D}$[5] about 3% as large as that of the starting olefin. Samples of (−)-II-Cl were prepared shortly before use and stored at 0°.

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(1) This research was supported by the National Institutes of Health (GM 14134) and the National Science Foundation (GP-21116X).

(2) H. C. Brown and L.-T. Liu, *J. Amer. Chem. Soc.*, **89**, 466 (1967).

(3) Incomplete reaction presumably results from encapsulation of liquid olefin by solid adduct. Evidently unreacted olefin did not interfere with the nmr analysis in the earlier work;[2] in the present work it was essential to obtain pure II-Cl.

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