ANGLES (DEG) DISTANCES (Å)

Figure 1. Bond distances and angles and their standard deviations in TCBD and DCBD. All molecules possess a crystallographic center of symmetry.

d(hkl)	I/I(o)	hkl
8.728	3	0 1 1
8.130	3	0 1 1
6.369	23	0 1 2
5.901	24	0 1 2
4.984	2	0 2 0
4.851	3	0 2 1
4.739	6	0 1 3
4.639	3	0 2 1
4.448	6	0 1 3
4.343	15	0 2 2
4.046	10	0 2 2
3.759	10	1 0 0
3.736	7	1 0 1, 0 2 3
3.578	50	1 0 1, 1 1 0
3.537	2	1 1 1, 0 1 4
3.456	60	1 1 0, 1 1 1
3.330	100	1 1 2
3.296	38	1 1 1, 0 3 1
3.266	23	1 0 2
3.188	25	1 0 3, 0 3 1
3.180	22	0 2 4
3.035	50	1 1 3, 0 1 5, 1 1 2
3.003	3	1 2 1
2.953	17	0 2 4
2.916	13	1 0 3
2.892	5	0 1 5, 1 2 2, 0 3 3
2.866	4	1 1 3
2.850	4	1 2 2

40 additional lines to 1.603 Å were recorded.

OCBD

d(hkl)	I/I(o)	hkl
9.9	13	0 0 1
6.55	25	0 1 0
5.00	63	0 1 1
4.39	5	0 1 2
3.56	63	1 1 0
3.46	25	1 1 1
3.26	100	1 0 1, 0 2 0, 1 1 1
3.01	10	0 2 2
2.92	20	0 2 1, 1 1 2
2.76	5	1 1 2, 1 2 0
2.57	8	1 1 3
2.48	8	1 1 4, 0 0 4
2.38	5	1 2 2
2.30	5	1 0 4, 1 1 2
2.21	5	0 3 1, 1 1 4
2.12	18	1 1 4, 1 2 3
2.07	5	1 3 0, 1 2 1
2.03	5	0 3 1

Figure 2. X-Ray powder diffraction data for TCBD and DCBD (courtesy of H. W. Rinn). The data for TCBD were obtained on a 115-mm diameter AEG (Allgemeine Elektrizitäts-Gesellschaft) Guinier camera using Seeman-Bohlin focusing and Cu $K\alpha_1$ radiation (λ 1.5405 Å). The DCBD data were taken with a 143.2-mm diameter Debye–Scherer camera using Cu $K\alpha$ radiation (λ 1.5418 Å).

squares molecular plane. In both crystals, the molecules form stacks along the short x axes. Because the normals to the molecular planes are tilted with respect to the translation direction (by 24.4° for TCBD-A,

Table I. Crystal Data

	TCBD	DCBD
Molecular formula	$C_{12}H_4O_2Cl_4$	$C_{12}H_6O_2Cl_2$
Molecular weight	321.977	253.086
Crystal habit	Lath	Lath
Long direction	a	a
Major faces	$\{01\bar{1}\}$	$\{010\}$
Crystal size, mm	1.30 × 0.396 × 0.072	1.50 × 0.022 × 0.096
Space group	$P\bar{1}$	$P\bar{1}$
Cell constants (25°)		
a, Å	3.783 ± 0.003	3.878 ± 0.003
b, Å	9.975 ± 0.009	6.755 ± 0.009
c, Å	15.639 ± 0.015	10.265 ± 0.015
α, deg	94.14 ± 0.02	99.46 ± 0.01
β, deg	95.20 ± 0.04	100.63 ± 0.03
γ, deg	92.77 ± 0.04	99.73 ± 0.03
Unit cell volume, Å³	585.3 ± 0.4	255.2 ± 0.1
Density (calcd), g cm⁻³	1.827 (Z = 2)	1.647 (Z = 1)
Linear absorption coeff (Mo $K\alpha$), cm⁻¹	9.79	5.26
No. of reflections measured	2666	1152
No. of reflections above background	2381	1030
$R_1 = \Sigma\|\|F_o\| - \|F_c\|\|/\Sigma\|F_o\|$	0.036	0.057
$R_2 = \{\Sigma w(F_o - F_c)^2/ \Sigma wF_o^2\}^{1/2}$	0.038	0.062

22.6° for TCBD-B, and 25.9° for DCBD), the distances between the molecular planes (3.446 Å for TCBD-A, 3.493 Å for TCBD-B, and 3.489 Å for DCBD) are

somewhat shorter than the corresponding lattice periods. Bond distances and angles, and their standard deviations, are given in Figure 1; their values show excellent internal consistency and also agree well with accepted literature values.[9] Further details of these structures will be published elsewhere.[10] The reader is also referred to the crystal structure of 1,2,3,7,8,9-hexachlorodibenzo-p-dioxin which has been reported by Cantrell, Webb, and Mabis.[11]

We have found X-ray powder diffraction to be very expeditious in identifying laboratory samples of chlorinated dioxins, and accordingly we give the observed powder patterns of 2,3,7,8-tetrachlorodibenzo-p-dioxin and 2,7-dichlorodibenzo-p-dioxin in Figure 2.

(9) L. E. Sutton, *Chem. Soc., Spec. Publ.*, No. 18 (1965).
(10) We have also recently completed the crystal structures of 2,8-dichlorodibenzo-p-dioxin (space group *Pnam*, a = 5.983 (6), b = 7.114 (10), c = 24.637 (36) Å, Z = 4) and octachlorodibenzo-p-dioxin (space group $P2_1/c$, a = 12.009 (9), b = 3.828 (3), c = 16.297 (9) Å, β = 101.14 (3)°, Z = 2).
(11) J. S. Cantrell, N. C. Webb, and A. J. Mabis, *Acta Crystallogr., Sect. B*, 25, 150 (1969).

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Reactions of Coordinated Nucleophiles. Formation and Structure of a Novel Tridentate Complex

Sir:

This publication reports a novel rapid reaction involving condensation of coordinated ligands to give a tridentate amidine. cis-[Co(en)$_2$(NH$_2$CH$_2$CN)Cl]$^{2+}$ reacts in near neutral or basic solution to give a purple complex with the constitution [Co(en)(NH$_2$CH$_2$C(NH$_2$)=NCH$_2$CH$_2$NH$_2$)Cl]$^{2+}$ (abbreviated I-Cl, ϵ_{max} 214 M^{-1} cm^{-1} at 552 nm, 25°, 1 M NaClO$_4$) where one end of a bidentate ethylenediamine ligand has con-
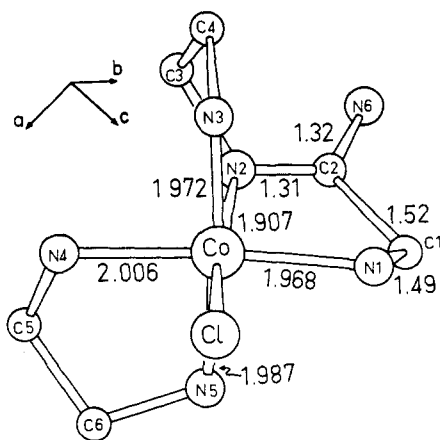
Figure 1.

densed with the bound NH_2CH_2CN moiety. The reaction is fast at pH 9 and 25° ($t_{1/2} \sim 4$ sec) and much faster than the base hydrolysis of Cl⁻ ion ($k_{25°} \approx 0.6$ $M^{-1} sec^{-1}$, $\mu = 1.0$ $NaClO_4$).

The structure of the condensation product has been elucidated by a three-dimensional X-ray structure analysis. Crystals of I-Cl dichloride monohydrate are orthorhombic, space group $P2_12_12_1$, $a = 8.473$, $b = 12.854$, $c = 13.807$ Å; $Z = 4$. *Anal.* Calcd for $CoCl_3H_{22}C_6N_6O$: C, 20.04; H, 6.17; N, 23.37; Cl, 29.58. Found: C, 20.0; H, 6.3; N, 23.1; Cl, 29.5. The crystal used was selected from a racemic mixture, and the relationship between its absolute configuration and rotatory dispersion curve will be established at a later date. The 1119 unique reflections with $I/\sigma(I) \geq 3.0$ were collected on a Picker FACS-I automatic diffractometer using monochromated Cu Kα radiation. Block-diagonal least-squares refinement of positional and isotropic thermal parameters for all atoms has converged to a conventional R of 0.075.[1]

The salient features of the structure are: (a) condensation has occurred at the N center trans to Cl⁻, resulting in a facial configuration for the tridentate ligand; (b) the amidine N(2)–C(2) (1.31 (2) Å) and amino N(6)–C(2) (1.32 (2) Å) distances are short, which suggests a bond order between 1 and 2 for both bonds; (c) the Co–N(2) (amidine) bond length, 1.907 (11) Å, is significantly shorter than the other Co–N bond lengths; (d) there is a striking distortion, especially of the apical ring (Figure 1) of the tridentate chelate. Moreover, both fused five-membered chelates are considerably distorted toward eclipsed conformations (C–H and amidine NH_2 and both sets of $>CH_2$ protons in an envelope form). The distortion in the vertical ring appears to arise from the attempt of the amidine N atom to achieve an sp^2 configuration (angles about this atom are C(2)–N(2)–C(3), 119.3 (11)°; Co–N(2)–C(2), 116.0 (9)°; Co–N(2)–C(3), 112.6 (8)°). The angles about the sp^2 carbon atom are N(2)–C(2)–C(1), 115.1 (11)°; C(1)–C(2)–N(6), 118.6 (12)°; N(2)–C(2)–N(6), 126.2, (12)°.

The formation of the complex I-Cl was followed spectrophotometrically in the pH range 7.31–8.94 (0.025 M tris(2-hydroxymethyl)aminomethane, $\mu = 1.0$ $NaClO_4$)

to give a rate law $\nu_{I-Cl} = k[Co][OH^-]$ where $k_{25°} = 1.64 \times 10^4$ M^{-1} sec^{-1}. The analogous I-Br complex was also prepared and gave a rate constant for the same process of 2.36×10^4 M^{-1} sec^{-1}. Neither complex consumed base in this reaction and the relatively broad $-C\equiv N$ stretching frequency at ~ 2370 cm^{-1} was replaced by a strong absorption at ~ 1660 cm^{-1}. At higher pH values hydrolysis of halide from each of these complexes occurred in a single rate process which indicates the material is isotropic. Moreover, the change in the pmr spectrum for the process nitrile → tridentate (pD 6.8) also indicated only one process and one product identical with the spectrum of the isolated product. Finally the optically pure cis-[Co(en)$_2$(NH$_2$-CH$_2$CN)Cl]Cl$_2$, [M]$^{25}_{589}$ +643°, [M]$^{25}_{523}$ −329°, was converted in solution to I-Cl, [M]$^{25}_{589}$ −2410°, [M]$^{25}_{523}$ +6680° (optically pure I-Cl, [M]$^{25}_{589}$ ±2550°, [M]$^{25}_{523}$ ±6865°), and the rotatory dispersion curve of the product (600–400 nm) agreed with that for the optically pure I-Cl (within 5%). These results indicate that the product from the reaction is one isomer ($\geqslant 95\%$) and a striking feature of the process, therefore apart from the rapid rate, is its stereospecificity since there are potentially three sites for condensation.

The mechanism proposed for the tridentate formation is deprotonation of the $-NH_2$ group trans to bound Cl⁻ (or Br⁻) followed by nucleophilic attack of coordinated amide at the nitrile C atom. Subsequent proton transfers give the "exo" $-NH_2$ group. The 100-MHz pmr spectrum in DMSO-d_6 of I-Cl shows that the signal for the exo N center at 8.4 ppm integrates for two protons. The large downfield shift relative to the other N protons is consistent with the charge delocalization over both amidine N groups. A pmr study showed that proton exchange was at least 40 times faster than cyclization and the rate-determining step must therefore be condensation. In pentaamine-type complexes akin to the reactant, the N protons trans to an anionic substituent exchange much faster (>50 times) than the N protons cis to the substituent.[2] It is likely therefore that the reaction is stereospecific because the $-NH$ center trans to Cl⁻ (or Br⁻) is by far the most abundant deprotonated form. This is the only reason we can see for the isomeric preference since it is probable that the isomer produced is one of the least stable possibilities. The structure gives a strong indication of the strain in the tridentate and it is certain that the least strained tridentate would be that where the fused rings are in the same plane. A strong analogy to support this assertion occurs with the bis(glycylglycinato)-cobalt(III) structures where the chelate is only found in the meridional form and where the structural features analogous to (b) and (c) are also observed.[3]

Additional experiments are now being conducted to explore the scope of this reaction in generating specific isomers, additional heterochelates, and macrocyclic chelates and to examine the base hydrolysis of the tridentate species.

It should also be added that after embarking on this study we found some results[4] reported on the same

(1) Corrections for anomalous scattering and slight crystal decomposition ($\sim 5\%$) have been included in the structure factor calculations. For the structure of inverse absolute configuration, the least-squares refinement converged to $R = 0.125$. Corrections for absorption have not yet been made.

(2) D. A. Buckingham, P. A. Marzilli, and A. M. Sargeson, *Inorg. Chem.*, **8**, 1595 (1969).

(3) M. T. Barnet, H. C. Freeman, D. A. Buckingham, I. N. Hsu, and D. van der Helm, *Chem. Commun.*, 367 (1970); G. B. Robertson, private communication.

(4) S. C. Chan and F. K. Chan, *Aust. J. Chem.*, **23**, 1175 (1970).

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

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

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

(3) A. C. Villa, A. G. Manfredotti, M. Nardelli, and C. Pelizzi, *ibid.*, 1322 (1970).

(4) The compound $Pt_2[P(C_6H_5)_3]_3S(CO)$ 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.
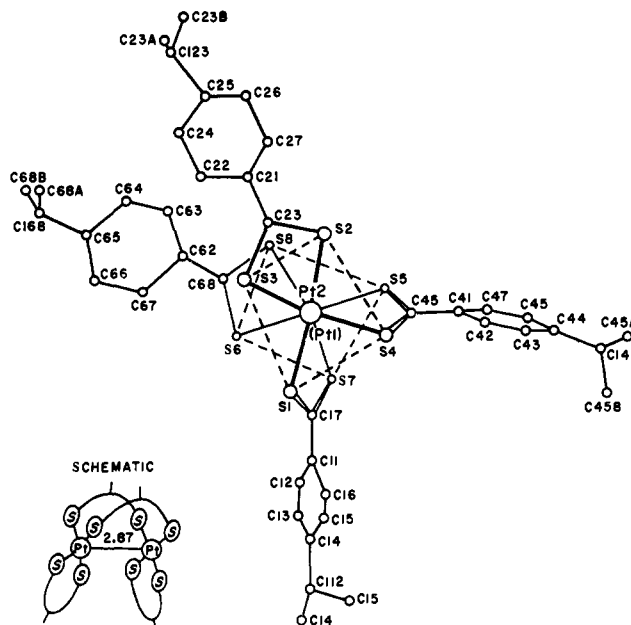

Figure 1. The molecular structure of $Pt_2(S_2CC_6H_4C_3H_7)_4$.

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.

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

(10) J. M. Burke and J. P. Fackler, Jr., to be submitted for publication.

(11) D. R. Swift, Ph.D. Thesis, Case Western Reserve University, 1970.

(12) D. Coucouvanis, S. J. Lippard, and J. A. Zubieta, *Inorg. Chem.*, 9, 2775 (1970).

(13) J. Lewis and R. S. Nyholm, *Sci. Progr.* (*London*), 52, 557 (1964); J. Lewis, *Pure Appl. Chem.*, 10, 11 (1965).

(14) K. Krogmann, *Z. Anorg. Allg. Chem.*, 332, 247 (1964); 358, 97 (1968).