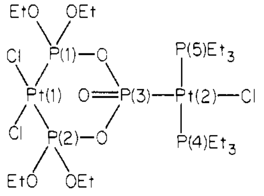
followed by evaporation of solvent and recrystallization of the residues from CH_2Cl_2/hexane, gave complex **1** as colorless



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crystals (0.13 g). The same product can be obtained by hydrolysis of *cis*-$[PtCl_2(PCl(OEt)_2)(PEt_3)]$ using aqueous HCl in acetone, but the course of this latter reaction is very sensitive to water and HCl concentration and the simple *cis*-$[PtCl_2(P(OH)(OEt)_2)(PEt_3)]$ is also a product. The basic form of **1** and the presence of the bridging triphosphite ligand was inferred from $^{31}P\{^1H\}$ and $^{195}Pt\{^1H\}$ NMR spectra (Figure 1) and subsequently confirmed by an X-ray crystal structure determination (Figure 2).

In the $^{31}P\{^1H\}$ NMR spectrum[8] the resonance at +20.0 ppm is assigned to the triethylphosphine ligands, P(4,5), and their mutually trans arrangement on a platinum(II) center is indicated by the magnitude of coupling to ^{195}Pt ($I = {}^1/_2$, 34% abundance), $^1J(Pt-P) = 2322$ Hz. The presence of P(3) in a cis relationship to the PEt_3 ligands is shown by the 1:1 doublet form of the P(4,5) resonance with $^2J(P-P) = 26$ Hz. The P(1,2) resonance centered at +50.3 ppm is associated with both direct ($^1J(Pt-P) = 5408$ Hz) and indirect ($^3J(Pt-P) = 94$ Hz) coupling to ^{195}Pt, the former value being typical of those found by us for a phosphite trans to chlorine, and is also coupled to a single phosphorus nucleus P(3) ($^2J(P-P) = 22$ Hz). This suggests the bridging arrangement, which is confirmed by the P(3) resonance at +37.0 ppm, which has the form expected for indirect coupling to two sets of equivalent pairs of ^{31}P nuclei and direct coupling to a single platinum ($^1J(Pt-P) = 6064$ Hz). Interestingly, P(3) is not significantly coupled to Pt(1).

The $^{195}Pt\{^1H\}$ NMR spectrum[9] confirmed the presence of two nonequivalent platinum nuclei (Pt(1), $\Xi = 21.403838$ MHz; Pt(2), $\Xi = 21.397700$ MHz) with couplings to phosphorus as expected from the above analysis and with $^4J(Pt-Pt) = 363$ Hz.

Crystals of **1** suitable for study by X-ray diffraction were obtained by crystallization from a dichloromethane/pentane solvent mixture.[10] Figure 2 shows that the overall structure is dictated by the six-membered ring linking the two platinum(II) centers. The ring lies in a *chaise-longue* conformation with O(1) and O(2) held in the same plane as the Pt(1) coordination. P(3) lies above this plane, and the Pt(2) coordination plane is approximately perpendicular (93.6°) to that of Pt(1). As expected, the shortest phosphorus–oxygen distance is the P(3)–O(3) double bond, 1.471 (9) Å. There are significant differences between the various P–O single bonds, with P^V–O(1,2), P^{III}–O(1,2), and P^{III}–OEt averaging 1.637 (9), 1.601 (8), and 1.565 (11) Å, respectively, but the Pt–P bonds do not appear to show any comparable effects. Thus, Pt(1)–P(1,2) averages 2.204 (3) Å and Pt(2)–P(3) is 2.198 (3) Å.

Our research is continuing in the designed synthesis of condensed phosphites, and full details will be published at a later date.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada and the University of Victoria for research grants, K. Beveridge for technical assistance during the crystal structure determination, and the University of Sussex for a study leave (A.P.).

Registry No. 1, 85762-22-7; $(EtO)_2POP(OEt)_2$, 21646-99-1; *trans*-$[Pt_2Cl_4(PEt_3)_2]$, 17522-94-0; *cis*-$[PtCl_2(PCl(OEt)_2)(PEt_3)]$, 85762-23-8.

Supplementary Material Available: Tables of fractional atomic coordinates and anisotropic thermal parameters (4 pages). Ordering information is given on any current masthead page.

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[8] $^{31}P\{^1H\}$ NMR spectra were recorded at 101.3 MHz, and chemical shifts are quoted in ppm (high field negative) relative to 85% H_3PO_4.

[9] $^{195}Pt\{^1H\}$ NMR spectra were recorded at 53.5 MHz and chemical shifts (Ξ) are quoted in MHz standardized to $[Si(CH_3)_4]$ at 100 MHz.

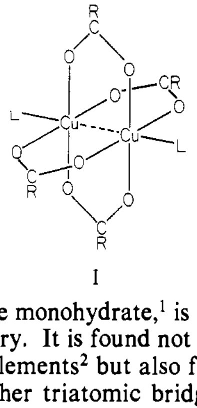
[10] The colorless crystals of the title compound, $C_{20}H_{50}Cl_3O_7P_5Pt_2$, are monoclinic, space group $P2_1/c$, with $a = 17.547$ (8) Å, $b = 19.775$ (6) Å, $c = 11.268$ (3) Å, $\beta = 106.42$ (3)°, $V = 3750$ (2) $Å^3$, $Z = 4$, and $\rho_{calcd} = 1.867$ g cm^{-3} (Mo Kα = 0.710 69 Å). The structure was solved and refined with use of 4646 independent reflections ($I > 0$) measured on a Picker four-circle diffractometer automated with a PDP-11/10 computer. The measurements were for two octants in the range $2\theta = 0$–45°. The platinum atoms were located by direct methods, and the structure was then developed and refined by Fourier difference maps and the method of least squares, anisotropic thermal corrections being applied to all non-hydrogen atoms. The crystal structure is molecular. Convergence (maximum shift/esd = 0.12) was attained at $R = 0.0612$, $R_w = 0.0726$. The final difference map had no interpretable peaks (maximum 1.83 e $Å^{-3}$ near Pt).

A Novel Variation on a Classical Dimeric Structure Type. Preparation and Structure of the Metal-Nitroxyl Complex $[Cu(O_2CCCl_3)_2(Tempo)]_2$

Sir:

We wish to report the preparation and crystal structure of a compound whose molecular structure is an unusual variant of a classic dimeric structure type and which contains one of the few structurally characterized examples of a metal-coordinated nitroxyl function.

The bridged binuclear structure I, first documented in 1953



I

for copper(II) acetate monohydrate,[1] is ubiquitous in modern coordination chemistry. It is found not only for carboxylates of many transition elements[2] but also for dimers containing a wide variety of other triatomic bridging ligands.[3] This structure is associated with a spectrum of metal–metal interactions ranging from no bonding at all[5] through weak spin

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[1] van Niekerk, J. N.; Schoening, F. R. L. *Acta Crystallogr.* **1953**, *6*, 227.

[2] For a tabulation, see: Koh, Y. B.; Christoph. G. G. *Inorg. Chem.* **1979**, *18*, 1122.

[3] A recent discussion and tabulation of such bridging ligands may be found in ref 4, pp 26–29.

[4] Cotton, F. A.; Walton, R. A. "Multiple Bonds Between Metal Atoms"; Wiley: New York, 1982.

[5] Larin, G. M.; Kalinnikov, V. T.; Aleksandrov, G. G.; Struchkov, Yu. T.; Pasnskii, A. A.; Kolobova, N. E. *J. Organomet. Chem.* **1971**, *27*, 53.

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Table I. Bond Distances and Angles about Copper Atoms

(a) Distances (Å)

Cu(1)-O(1)	1.917 (8)	Cu(2)-O(2)	2.289 (9)
Cu(1)-O(3)	2.302 (9)	Cu(2)-O(4)	1.896 (9)
Cu(1)-O(5)	1.905 (8)	Cu(2)-O(6)	2.129 (8)
Cu(1)-O(7)	2.055 (9)	Cu(2)-O(8)	1.920 (8)
Cu(1)-O(9)	1.942 (8)	Cu(2)-O(10)	1.950 (8)

(b) Angles (deg)

O(1)-Cu(1)-O(3)	86.8 (4)	O(2)-Cu(2)-O(4)	88.0 (4)
O(1)-Cu(1)-O(5)	172.9 (4)	O(2)-Cu(2)-O(6)	126.5 (3)
O(1)-Cu(1)-O(7)	93.3 (4)	O(2)-Cu(2)-O(8)	89.6 (4)
O(1)-Cu(1)-O(9)	94.6 (4)	O(2)-Cu(2)-O(10)	112.5 (4)
O(3)-Cu(1)-O(5)	86.3 (4)	O(4)-Cu(2)-O(6)	91.2 (4)
O(3)-Cu(1)-O(7)	124.8 (4)	O(4)-Cu(2)-O(8)	177.6 (4)
O(3)-Cu(1)-O(9)	106.1 (4)	O(4)-Cu(2)-O(10)	94.6 (4)
O(5)-Cu(1)-O(7)	91.9 (4)	O(6)-Cu(2)-O(8)	90.5 (3)
O(5)-Cu(1)-O(9)	85.9 (4)	O(6)-Cu(2)-O(10)	120.9 (4)
O(7)-Cu(1)-O(9)	128.9 (4)	O(8)-Cu(2)-O(10)	86.0 (3)

pairing in the copper(II) carboxylates[6] and on through the various orders of metal–metal covalent bonding to the "supershort" interactions which represent the very shortest of all metal–metal bonds found in isolable molecules.[7] Associated with this spectrum of interactions are bond distances ranging from 3.70 Å in a vanadium cyclopentadienyl trifluoroacetate dimer[5] to 1.828 (2) Å in a chromium dimer bridged by the 2-methoxy-5-methylphenyl anion.[8] The axial ligand L may be absent or may represent interdimer association into a polymeric structure.

In the classical copper(II) acetate structure, the environment of the metal atom is square planar or square pyramidal. The axial ligand, if present, is bound to the metal atom by a bond significantly longer than those to the atoms occupying basal sites. For example, typical basal and axial Cu-O distances in the copper(II) carboxylate dimers are ca. 2.0 and 2.15 Å, respectively.[6] With minor distortions and variations, this general pattern has been found in all of the many bridged dimers of structure type I studied to date.

In the course of our studies of the ligand behavior of the nitroxyl function,[9–11] we have found an adduct with the usual $[Cu(O_2CR)_2L]_2$ stoichiometry and tetrabridged structure but with an unexpected copper coordination geometry and a novel configuration for two of the four carboxylate bridges.

From a pentane solution containing equimolar amounts of anhydrous copper(II) trichloroacetate and the stable nitroxyl radical 2,2,6,6-tetramethylpiperidinyl-1-oxy (Tempo) was obtained a deep green crystalline sample of $[Cu(O_2CCCl_3)_2(Tempo)]_2$. Elemental analyses (C, H, N, O) were in good agreement with the monoadduct stoichiometry. The crystal structure was determined by single-crystal X-ray methods.[12,13]

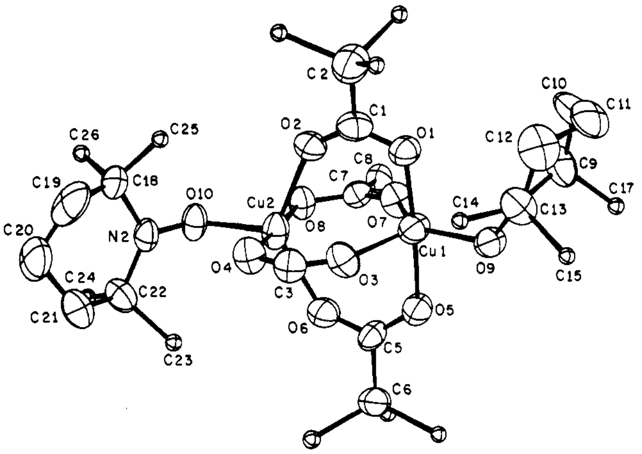

Figure 1. View of the molecular structure of $[Cu(O_2CCCl_3)_2(Tempo)]_2$. In order to show clearly the copper coordination geometry and the carboxylate bridges, the chlorine atoms bound to C(2) and C(6) and the Tempo methyl carbon atoms have been given artificially small thermal parameters. Also, the chlorines bound to C(8) and the entire CCl_3 group on C(3) have been omitted. The nitrogen atom N(1) (bound to O(9)) is obscured in this view; the geometries of binding of the two Tempo ligands closely resemble each other.

A view of the molecular structure of bis(2,2,6,6-tetramethylpiperidinyl-1-oxy)tetrakis(μ-trichloroacetato-*O,O′*)dicopper(II) is shown in Figure 1. Bond distances and angles involving the copper atoms are listed in Table I. Although this molecule has the same stoichiometry and atomic connectivity as the classic dimer structure I, the geometry of its central portion differs *qualitatively* from that which is normally found. The angular geometry about each of the two crystallographically independent copper atoms closely approximates that of a trigonal bipyramid; in fact, the mean deviation of the coordination angles from their ideal trigonal-bipyramidal values is less than 4°. The coordination polyhedra of Cu(1) and Cu(2) are quite similar, but their axial directions (defined by the O(1)–O(5) and O(4)–O(8) vectors) are approximately perpendicular to each other.

Bond length patterns are also unusual. The two nitroxyl oxygen atoms are bound to copper by short bonds (Cu(1)–O(9) = 1.942 (8) Å; Cu(2)–O(10) = 1.950 (8) Å) much like those in the Tempo adduct of bis(hexafluoroacetylacetonato)copper(II).[9] One of the *equatorial* Cu–O bonds to each copper is very long—Cu(1)–O(3) = 2.302 (9) Å and Cu(2)–O(2) = 2.289 (9) Å. Consequently, there are two inequivalent types of bridging carboxylate—two highly asymmetric ones with one very long Cu–O distance and two with more normal, but still unequal, metal–oxygen distances. The Cu–Cu distance is 3.256 (2) Å, far longer than in any other dimeric copper(II) carboxylate adduct.[6]

This compound is also of considerable interest as one of the very few structurally characterized examples of molecules containing a covalent metal–nitroxyl bond. Two crystal structures of such compounds have recently been reported,[9,14] and we have found a few other examples.[15] Several recent attempts to prepare metal complexes with covalently bound nitroxyl ligands have yielded crystalline products in which the nitroxyl group is noncoordinated.[11,15,16] Clearly, the factors influencing whether a nitroxyl group will bind to a transition-metal center remain poorly understood.

Finally, the magnetic properties of this material will be of considerable interest because it contains four paramagnetic centers, a metal–nitroxyl bond, and a new type of carboxyl-

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(12) Crystal data for $Cu_2C_{26}H_{36}O_{10}N_2Cl_{12}$: fw 1089.1; monoclinic, $P2_1/n$; a = 12.134 (3), b = 22.465 (5), c = 16.693 (3) Å; β = 100.43 (2)°; Z = 4; V = 4475.4 (17) Å^3; ρ_{obsd} = 1.62 g cm^{-3}, ρ_{calcd} = 1.65 g cm^{-3}. The structure determination was based upon 4100 independent nonzero data with $(2\theta)_{max}$ = 50° collected on a Syntex $P2_1$ diffractometer with monochromatized Mo Kα radiation. The general procedures used in data collection and reduction have been described: Sams, D. B.; Doedens, R. J. *Inorg. Chem.* **1979**, *18*, 153.

(13) The crystal structure was solved by direct methods and refined by full-matrix least-squares techniques to a final conventional R factor of 0.090. The higher than normal final value of R is a consequence of some unresolved disorder and/or high amplitude thermal motion of the CCl_3 groups. Simple disorder models did not alleviate this problem. Computer programs used were those of a locally modified version of the UCLA Crystallographic Computing Package (Strouse, C. E., personal communication). Full crystallographic details will be published at a later date when magnetic studies now in progress are completed.

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ate-bridged Cu(II)–Cu(II) linkage.

Registry No. $[Cu(O_2CCCl_3)_2(Tempo)]_2$, 85803-18-5.

Supplementary Material Available: Tables of atomic positional parameters, observed and calculated structure factors, elemental analysis, anisotropic thermal parameters, and bond distances and angles (25 pages). Ordering information is given on any current masthead page.

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Received March 8, 1983

Quadruple Probing of Electronic Excited States by Magnetic Circular Dichroism (MCD), Linearly Polarized Luminescence (LPL), Linearly Polarized Excitation Luminescence (LPEL), and Optical Absorption Techniques: Pentacarbonyl(piperidine)tungsten(0), $W(CO)_5pip$

Sir:

Our laboratory[1,2] and another[3] have very recently shown that electronic absorption polarizations can be assigned directly for ${}^1E \xleftarrow{\sigma} {}^1A_1$ excitations of synthetically and photochemically important tetragonal six-coordinate transition-metal carbonyl complexes $M(CO)_5L$ (e.g., M = Cr, Mo, W; L = amines, phosphines, stibines, arsines) in optically *isotropic solutions.* Solution MCD spectroscopy was used for this purpose, and the quantum interpretation of the signs of Faraday A terms by means of reliable orbital angular momentum calculations of signs of $\langle L \rangle$ for excited states made possible the assignment of MO fates for one-electron excitation processes. These and indirect considerations led to this excited-state assignment of $W(CO)_5L$[1,2] in order of increasing energy (I < II < III):

I ${}^3E[a_1{}^1(\sim d_{z^2})e^3(\sim d_{xz},d_{yz})] \leftarrow$
${}^1A_1[e^4(\sim d_{xz},d_{yz})]$ ~440 nm

II ${}^1E[a_1{}^1(\sim d_{z^2})e^3(\sim d_{xz},d_{yz})] \leftarrow$
${}^1A_1[e^4(\sim d_{xz},d_{yz})]$ ~400 nm

III ${}^1A_2(T_{1g})[b_1{}^1(\sim d_{x^2-y^2})b_2{}^1(\sim d_{xy})] \leftarrow$
${}^1A_1[b_2{}^2(\sim d_{xy})]$ ~340 nm

However, direct MCD-based polarization assignments availing excited-state symmetries of bands such as ${}^1A_2 \leftarrow {}^1A_1$ (band III, vibronically electric dipole allowed) or

$$ {}^1A_1 \xleftarrow[z]{\pi} {}^1A_1 $$

(electric dipole axially z allowed, molecular C_4 and z axes coincident) cannot in general be made reliably for large molecules such as the present one and others. Such interpretations of Faraday B terms[4] involve summations over all virtual states (k) (spectators during specific state excitation, j ← a) and involve electric $\langle er \rangle$ and magnetic $\langle L \rangle$ dipole integral evaluations (magnitudes and signs) that include spectator state functions $|k\rangle$, and $|a\rangle$ and $|j\rangle$, and the virtual MO's of $|k\rangle$ and $|j\rangle$, about nearly all of which little is known with certainty; also required for the B term evaluations are pure guesses about the correct one-to-one associations of ill-characterized excited-state and MO functions with spectator optical band energies, and many of these latter functions are not known at all in the vacuum-UV, for example.

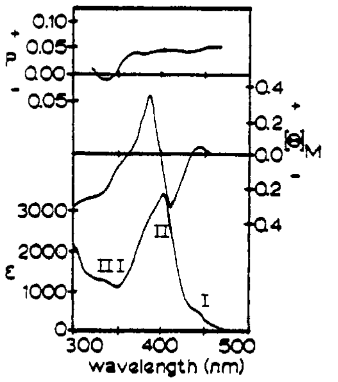

Figure 1. MCD (θ), LPEL (P), and optical spectra of $W(CO)_5pip$ (MCD and optical spectra at room temperature, LPEL spectrum at 80 K). $[\theta]_M$ is the molar ellipticity in a field of 1 G, ϵ the molar absorptivity, and P the degree of polarization ($P = (I_\parallel - I_\perp)/(I_\parallel + I_\perp)$). At 80 K about $^2/_3$ of band I is completely free of the tail of band II.

Reasons such as the above prompted us to measure the linearly polarized luminescence (LPL) and linearly polarized excitation luminescence (LPEL) on our laboratory's computerized modular instrument of original design. *Combining* LPL–LPEL results with MCD and optical data then led to new assignments as described. The LPEL–LPL instrument consists of CW xenon-lamp excitation (chopped), stepper motor driven excitation ($^1/_4$ m) and emission ($^1/_4$ m, double dispersion) grating monochromators, order filters, UV–visible–near-infrared polarizers, a wavelength-slaved electrooptic modulator, dual lock-in phase-sensitive detection, and a microprocessor for control of monochromators and modulator, collection of voltage-to-frequency converted PMT signals, and multiscan averaging. Operating at 50 kHz, the modulator on alternate half-cycles samples $I_\parallel$ and $I_\perp$ of emitted light, which becomes incident on a fixed polarizer (P2) preceding the emission monochromator. P2 passes vector projections of $I_\parallel$ and $I_\perp$. The LPEL–LPL spectra are precisely free of monochromator and detector anisotropy effects and of detector dark current. We sought linear polarization data from LPEL–LPL especially for the nondegenerate excited states, e.g., $A_1 \xleftrightarrow{\pi} A_1$, or electric dipole vibronically allowed states, e.g.

$$ A_2(a_2{}^{vib} \text{ or } e^{vib}) \xleftarrow{\sigma \text{ or } \pi} A_1 $$

Our aspiration was realized by executing the following plan.

The molecular excitation polarization of band II (~400 nm) was already known to be $\sigma(x,y)$, or ${}^1E \leftarrow {}^1A_1$, from the MCD.[1-3] Then the LPEL–LPL excitation and emission monochromators were set, respectively, to 400 nm (${}^1E \leftarrow {}^1A_1$) and 535 nm (emission maximum[5] at 80 K). The degree of linear emission polarization,[6] P, of the frozen solution was found to be positive and ca. 0.05 (Figure 1), indicative of dominant $\sigma(x,y)$ emission, or $\bar{E}({}^3E) \rightarrow A_1$. $\bar{E}$ is one of the spin–orbit components ($\bar{E}$, $\bar{A}_1$, $\bar{A}_2$, $\bar{B}_1$, $\bar{B}_2$) of ${}^3E$ mentioned above. *The direct finding that this emission is molecularly in plane, $\sigma(x,y)$, polarized at 535 nm is a new observation,*

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(4) B terms are given by

$$ B_{j \leftarrow a} = \sum Im \left[\sum_{k \neq a} \frac{\langle k|u|a \rangle}{(E_k - E_a)} \cdot \langle a|m|j \rangle \times \langle j|m|k \rangle + \sum_{k \neq j} \frac{\langle j|u|k \rangle}{(E_k - E_j)} \cdot \langle a|m|j \rangle \times \langle k|m|a \rangle \right] $$

where $u = L + 2S$ and $m = er$ for the valence electrons.

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