Comments on Inorganic Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455155

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To cite this Article Bellitto, Carlo(1988) 'Linear-Chain Dithiocarboxylato Complexes of the Nickel Triad: An Overview', Comments on Inorganic Chemistry, 8: 3, 101 — 124
To link to this Article: DOI: 10.1080/02603598808035788
URL: http://dx.doi.org/10.1080/02603598808035788

Linear-Chain Dithiocarboxylato Complexes of the Nickel Triad: An Overview

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Recent extensive research into the synthesis of transition metal dithiocarboxylates has led to the preparation and characterization of several linear-chain dithiocarboxylato complexes of the nickel triad in both single and mixed-valence state. The chemical, structural and physical properties of these compounds are presented and discussed.

Key Words: *one dimensional, metal dithiocarboxylates, crystal structure, mixed valence, optical, electrical properties*

INTRODUCTION

In the last decade substantial chemical effort has been devoted to the synthesis and characterization of one-dimensional (1D) transition metal complexes, especially the electrically conducting ones, as described recently by several authors.[1]

The interest lies in novel chemical and physical properties shown by these compounds. Several of these properties have been under-

Comments Inorg. Chem.
1988, Vol. 8, No. 3, pp. 101–124
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stood and some of them used for technological applications,[2] while others are still the subject of further studies.[3] In this context we decided a few years ago to focus our attention on new 1D materials containing transition metal ions, especially from the synthetic point of view. In particular, we have synthesized and studied several linear-chain derivatives of the nickel triad metals with 1,1 dithiocarboxylic acids having formula R-CS_2H,[4] where R is an alyphatic group.

This class of transition metal complexes is interesting because they contain chains of metal ions. It is important to mention that the nature of the substituent R in the dithioacid plays a crucial role in the formation of linear-chain systems. In fact, when R is an aryl group, the compound does not have a linear chain structure, but it crystallizes as oligomeric aggregates.[5] As found in more famous examples of 1D compounds,[6] two major chemical factors have been identified as important in relating structure and physical properties. The first is the presence or absence of a bridging group and the second is the problem of single or mixed oxidation state. With this in mind, we first will deal with single-valence compounds and then with mixed-valence compounds.

This survey emphasizes chemical aspects: it reviews the preparation and the structural and electronic properties of these compounds and it discusses the change of some relevant solid state properties in mixed-valence derivatives compared to the single-valence ones.

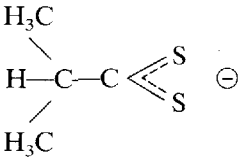
SINGLE-VALENCE COMPOUNDS

Synthesis

Tetrakis(dithiocarboxylato)diplatinum(II) is readily prepared by reaction of K_2PtCl_4 with the dithiocarboxylic acid in toluene under reflux in an inert atmosphere, during which the color of the reaction mixture changes from orange to dark-red. After filtration of the hot mixture, the filtrate on cooling gives needles showing copper luster. In the case of tetrakis(dithioisobutanoato)-diplatinum(II) two polymorphic forms have been isolated:[7]

$$K_2PtCl_4 + 2\ LH \xrightarrow[\text{reflux}]{\text{toluene}} 1/2\ Pt_2L_4 + 2\ HCl + 2\ KCl$$

where L is:



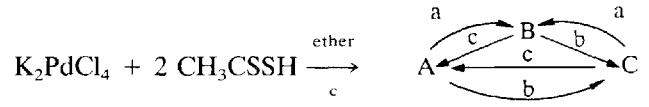
and

$$Pt_2L_4 \rightleftharpoons Pt_2L_4$$

A form B form

The first one, the A form, crystallizes upon cooling the filtrate, obtained from the reaction of a mixture of K_2PtCl_4 and the corresponding acid. The second one, the B form, is obtained from a carbon disulphide solution of the A form, by evaporation to dryness under inert atmosphere. All the dithiocarboxylato platinum derivatives are stable in air, but they decompose slowly after days of air exposure.

The dithioacetato palladium(II) compound exists in three distinct forms.[8] They correspond to a common 2:1 ligand-to-metal ratio, but they display different structures and optical spectra:



A form = $Pd_2(CH_3CS_2)_4 \cdot Pd(CH_3CS_2)_2$

B form = $Pd_2(CH_3CS_2)_4 \cdot CS_2$

a = crystallization in presence of CS_2.

b = sublimation.

c = crystallization from toluene, CH_2Cl_2.

SCHEME I

The red form A corresponds to the chemical formula $Pd(CH_3CS_2)_2 \cdot Pd_2(CH_3CS_2)_4$ and is obtained by a direct reaction of K_2PdCl_4 and of the dithioacetic acid in toluene, under reflux. The red-solid is recrystallized from toluene giving brick-red needle-like crystals.

The green B form corresponds to the chemical formula $Pd_2(CH_3CS_2)_4 \cdot CS_2$ and is obtained upon dissolution of the A form in CS_2 at ambient temperature. The resulting red solution almost instantly becomes turbid and in a few minutes a green microcrystalline solid separates. The third form, the C form, is obtained as bright-red microcrystalline material by sublimation of A or B forms. All these compounds are soluble or slightly soluble in nonpolar or weakly polar organic solvents such as benzene, toluene, chloroform or carbon disulphide. The solubility increases with the increase of the number of carbon atoms in the substituent R of the ligand. The nickel derivatives were all synthesized by mixing an ethanolic solution of $NiCl_2 \cdot 6\ H_2O$ with a solution of the corresponding acid.[9] The compound precipitates immediately as a dark-brown microcrystalline powder. Crystals suitable for X-ray studies are obtained by recrystallization from a carbon disulphide solution.

Structural Properties

The structural properties of M(II) dithiocarboxylates, where M = Ni, Pd, Pt, have been reported previously and are summarized in Table I.

As mentioned earlier, tetrakis(dithioisobutanoato)diplatinum(II) complex occurs in two polymorphic forms. The first one, of copper luster, crystallizes in the orthorhombic space group *Pccn*. It contains columnar stacks of binuclear units $[Pt_2S_8]$ as reported in Fig. 1. The platinum atoms lie on two-fold axes and the dimeric units are formed between two adjacent atoms in a bridged cage structure. Two different short Pt–Pt distances are present along the two-fold axis : Pt(1)–Pt(2), inside the dimer, is 2.795 Å, and Pt(2)–Pt(1'), between adjacent dimers, is 3.081 Å. Each platinum is surrounded by pairs of sulphur atoms in a square-planar arrangement, at an average Pt–S distance of 2.31 Å. The two $[PtS_4]$ units are rotated by 45° from the eclipsed structure. The second form, the green form, crystallizes in the tetragonal space group *I*4/*m*. The full crystal structure has not been solved owing to the statistical disorder of the sulphur and carbon atoms. The existence of platinum chains is proved from oscillation photographs, where only the $l = 2n$ layers are strong, and the Pt atoms are stacked along the four-fold axis at $c/2$. The intradimeric Pt–Pt distance has been estimated from Patterson map to be 2.76 Å and consequently a Pt interdimeric distance of 3.49 Å. A similar structure

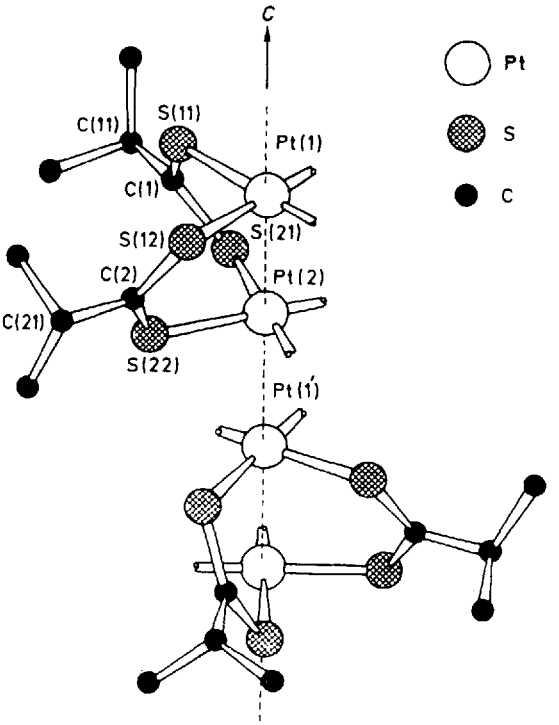


FIGURE 1 A view of a part of crystal structure of $Pt_2[(CH_3)_2CHCS_2]_4$, form A. (From Ref. 7, reproduced by permission.)

has been found for tetrakis(dithiophenylacetato)diplatinum(II)[10] and more recently for tetrakis(dithioheptanoato)diplatinum(II).[11] The crystal structure of tetrakis(dithioacetato)diplatinum(II) is slightly different and is reported in Fig. 2. It consists of dimeric units $[Pt_2S_8]$ stacking along the crystallographic *c* axis of the monoclinic space group $P2_1/n$, but the stacking is not collinear, the dimers being inclined with respect to the [001] direction by 28°.[12] The separations between Pt atoms of adjacent dimers are 3.819(1) and 3.776(1) Å. In the case of palladium derivatives, the structures of the two compounds have been solved. The crystal structure of the A form consists of mononuclear and binuclear units alternating along the *a* axis with metal repeat separations of 2.754(1) Å, inside the dimer, and 3.399(1) Å, between the Pd of the monomer and that of the dimer (see Fig. 3). The other crystal structure consists

TABLE I

Lattice parameters of tetrakis(dithiocarboxylato)metal(II) complexes, M = Ni, Pd, Pt.

Compound	Color	Crystal System	Lattice Parameters (Å)	Type of Stacks	M–M Separation *intra* (Å)	M–M′ Separation *inter* (Å)	Ref.
$Pt_2(CH_3CS_2)_4$	copper luster	monoclinic $P2_1/n$	a = 8.919(3) b = 16.628(4) c = 12.740(3) β = 110.40(4)°	M–M not collinear	2.767(1)	3.819(1) 3.776(1)	12
$Pt_2(C_6H_5CH_2CS_2)_4$	dark-green	orthorhombic *Iba*2	a = 9.345(4) b = 29.563(5) c = 12.005(2)	M–M	2.764(1)	3.238(1)	10
$Pt_2(n\text{-}C_6H_{13}CS_2)_4$	copper luster	monoclinic $C2/c$	a = 36.046(10) b = 6.079(1) c = 17.910(3) β = 92.49(2)°	M–M	2.855(1)	3.224(1)	11
$Pt_2(Pr^i\text{-}CS_2)_4$ form A	copper luster	orthorhombic *Pccn*	a = 9.947(4) b = 22.379(9) c = 11.752(2)	M–M	2.795(2)	3.081(2)	7
$Pt_2(Pr^i\text{-}CS_2)_4$ form B	dark green	tetragonal *I*4/*m*	$a = b$ = 14.477(4) c = 6.247(1)	M–M	2.76(1)	3.49(1)	10

$Pt_2(Pr^i\text{-}C_6H_5CS_2)_4$	dark green	triclinic	a = 15.564(6) b = 15.480(6) c = 12.555(3) α = 90.85(1)° β = 116.80(1)° γ = 122.55(1)°	–	2.870(1)	–	17
$Pd_2(C_6H_5CH_2CS_2)_4$	dark brown	orthorhombic *Iba*2	a = 9.334(5) b = 29.592(5) c = 12.023(5)	M–M	2.715(3)	3.297	13
$Pd_2(CH_3CS_2)_4 \cdot CS_2$	green	tetragonal *P*4/*ncc*	$a = b$ = 12.803(2) c = 11.995(2)	M–M	2.738(1)	3.257(1)	8
$Pd(CH_3CS_2)_2 \cdot Pd_2(CH_3CS_2)_4$	brick-red	monoclinic *C*2/*c*	a = 9.553(2) b = 17.875(2) c = 16.141(2) β = 107.30(1)°	M–M	2.754(1)	3.399(1)	8
$Ni_2(CH_3CS_2)_4$	red-brown	triclinic *P*1	a = 9.017(3) b = 9.098(3) c = 11.272(4) α = 105.07(2)° β = 67.67(2)° γ = 93.44(2)°	slipped stack	2.564(1)		14
$Ni_2(C_6H_5CH_2CS_2)_4$	red-brown	orthorhombic *Iba*2	a = 9.232(3) b = 29.420(7) c = 12.097(3)	M–M	2.551(3)	3.497	13
$Ni_2(Pr^i\text{-}CS_2)_4$	red-brown	not solved					

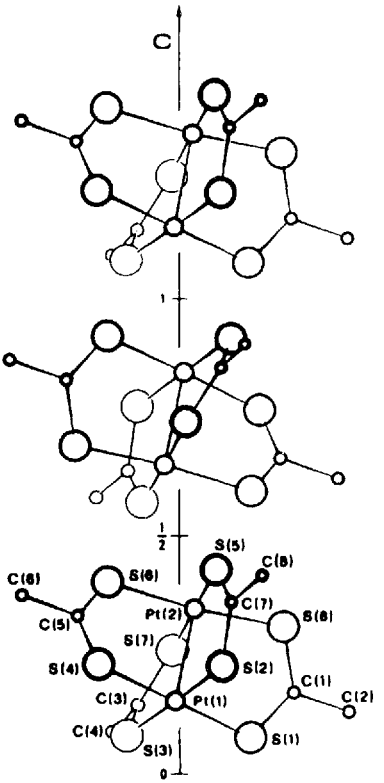


FIGURE 2 Stacking of the $Pt_2(CH_3CS_2)_4$ units along the c axis. (From Ref. 12, reproduced by permission.)

of dimers only, stacking along the four-fold axes of the tetragonal space group $P4/ncc$, with CS_2 molecules incorporated between different columns. In this case the intra- and the interdimeric Pd–Pd distances are 2.738(1) Å and 3.257(1) Å, respectively. A similar columnar structure is present in $Pd_2(C_6H_5CH_2CS_2)_4$.[13] Solid nickel dithiocarboxylato complexes also occur as dinuclear $[Ni_2S_8]$ units. In $Ni_2(C_6H_5CH_2CS_2)_4$ the intradimeric Ni–Ni distance is 2.56 Å. The molecules stack along the two-fold c axis of the unit-cell, with an interdimeric metal–metal distance of 3.50 Å.[13] The other known crystal structure is that of the tetrakis(dithioacetato)dinickel(II).[14] In this case the molecules are in a "slipped stack" arrangement.

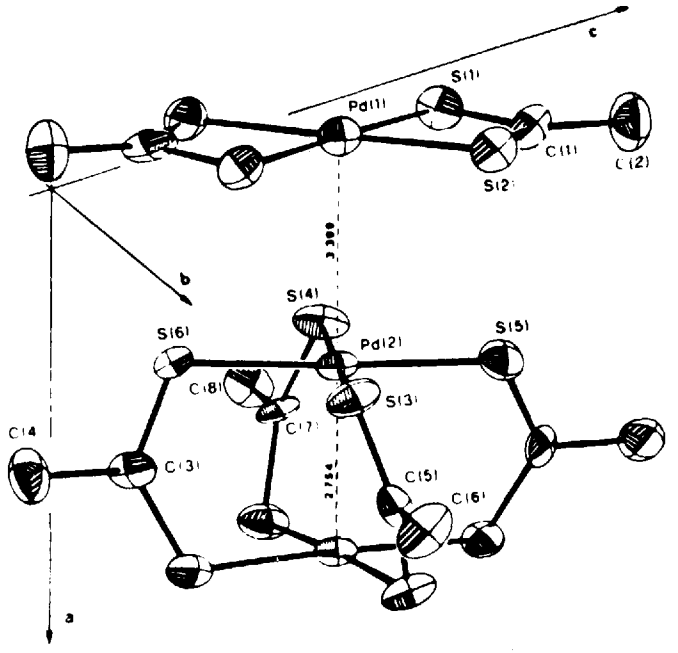


FIGURE 3 Illustration of $Pd(CH_3CS_2)_2$, form A, showing the molecular unit geometry and the Pd–Pd distance. (From Ref. 8, reproduced by permission.)

Except for the A form of the palladium dithioacetato complex, the building unit in these compounds is represented by a dimer $[M_2S_8]$. The molecular geometries are similar and the M–M intradimeric distance is short. In the case of the Pt derivatives, it varies between 2.76 and 2.85 Å. These values are comparable to the Pt–Pt distances observed in other reported dimeric systems such as $K_4[Pt_2H_8P_8O_{20}]\cdot 2\ H_2O$ [15] and the head to tail and head to head isomers of $Pt_2[(NH_3)_4(C_5H_4NO)_4]^{2+}$.[16] In general this short distance can arise both from the existence of a strong metal–metal bond and/or the constraint due to the bridging ligand, even when a direct metal–metal bond is of low formal order or nonexistent. This point will be discussed later in connection with the electronic structure. Similar considerations can be described for the nickel and palladium derivatives. As regards the linear chain structure, the interdimeric and the interchain distances are modulated by the substituent R of the ligand (see Table I). The other known plat-

inum columnar compound, where chains of dimers are present, is the octaphosphitediplatinum(II), i.e., $K_4[Pt_2H_8P_8O_{20}]\cdot 2\ H_2O$,[15] although the metal–metal distance between adjacent units $[Pt_2P_8]$ is much longer, i.e., 5.063 Å. In conclusion, the stacking of the molecules seems to be the most favorable packing in the solid state in the case of Pd and Pt derivatives. The reason for this lies in the fact that strongly directed nd_z2 and $(n + 1)p_z$ metal orbitals are best suited for intermolecular metal–metal overlap, when M–M stack is present. The strongest overlap of these orbitals occurs along the metal chains and it depends on the extension of the metal *d* orbitals. The latter is an important molecular parameter in favoring the direct stacking, but it is not the only one. The packing forces play an important role, if we take the example of $Pt_2[(p\text{-}Pr^i\text{-}C_6H_4CS_2)]_4$.[17] The complex is still dimeric, but the molecular units, with two bridging and two terminal dithiocarboxylato ligands, are not stacked in the unit-cell. The second example is represented by the canted structure of tetrakis(dithioacetato)diplatinum(II), described previously. Finally, the individual chain is very well separated from the adjacent ones by the ligands, and the distance depends on the hindrance of the substituent R. In some complexes the molecules of one chain are shifted in the direction of the *c* axis with respect to the neighboring chain.

Oligomeric Species

There is recent experimental evidence for the presence of clusters of $M_2(RCS_2)_4$ in concentrated toluene solutions, at lower temperatures, probably as precursors of chain formation.[11] A reversible dimerization due to the equilibrium monomer $\rightleftarrows$ dimer has also been observed.[8,11].

The electronic structure of $M_2(RCS_2)_4$ molecule, where M = Ni, Pd, Pt

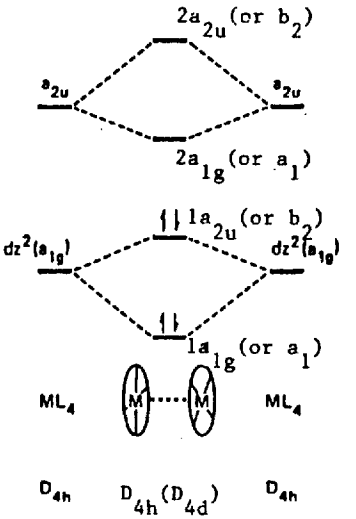
The solid state properties of the linear chain compounds are mainly determined by the electronic structure of the binuclear $M_2(RCS_2)_4$ molecule. An ab-initio calculation of the electronic structure of this molecules does not exist, due to the complexity of the system. Concerning the optical properties, however, the highest occupied (HOMO) and lowest unoccupied (LUMO) molecular orbitals con-

stitute the points of major interest. Thus, it is possible to restrict drastically the number of electrons and states compared to the full problem. An approximate LCAO-MO-SCF method has been applied to palladium dithioacetato compounds.[18] Following this calculation in $Pd_2(CH_3CS_2)_4$, the relative ordering of the "*d*-like" orbitals is:

$$4d_{xy} > 4d_{z^2} > 4d_{yz} > 4d_{xz} > 4d_{x^2-y^2}$$

with the ground state of $^1A_1$, the d_{z^2} being the main component of the HOMO orbital. Concerning the dinuclear unit $Pd_2(CH_3CS_2)_4$, it has been found that the MO's of $5p_z$ character are among the lowest virtual orbitals and that $4d_{z^2}$ mainly contributes to the highest-energy filled MO's.

More easily and approximate way of visualizing the various excited configurations for the binuclear complexes has been proposed by H. B. Gray *et al.*[19] and is reported in Scheme II:



SCHEME II

This scheme can also be applied to our systems. D_{4h} is assumed for simplicity and the relevant levels of the monomer $[MS_4]$ are

TABLE II

Comparison of geometric properties of various metal dithiocarboxylato derivatives

Compound	M–M (Å)	M–S (Å)	M–L (Å)	Metal Oxidation State	Ref.
$Pt_2(CH_3CS_2)_4$	2.767(1)	2.317(4)		II	12
$Pt_2(CH_3CS_2)_4I$	2.667(2)	2.324(6)	2.981(3)	II–III	28
$Pt_2[(CH_3)_2CHCS_2]_4$ form A	2.795(2)	2.306(6)		II	7
$Pt_2[(CH_3)_2CHCS_2]_4I_2 \cdot I_2$	2.578(1)	2.34	2.763(2)	III	20
$Pt_2[C_6H_5CH_2CS_2]_4$	2.761(2)	2.316(5)		II	10
$Pt_2[C_6H_5CH_2CS_2]_4I_2$	2.598(2)	2.329(6)	2.753(3)	III	20
$Mo_2(CH_3CS_2)_4 \cdot 2THF$	2.141(1)	2.468(5)		II	35
$Mo_2(C_6H_5CS_2)_4 \cdot 2THF$	2.139(2)	2.456(5)		II	35

also reported in the Scheme II. In a d^8-d^8 system, therefore, the highest occupied (HOMO) level is the $d\sigma^*$, $1a_{2u}$, and the ground state is ^1A_g. The lowest unoccupied orbital (LUMO) is the $p\sigma$, $2a_{1g}$. It is worthwhile mentioning that the oxidative addition of halogens to tetrakis(dithiocarboxylato)diplatinum(II) complexes gives compounds of general formula $Pt_2(RCS_2)_4X_2$, where the Pt atoms are in the oxidation state +3.[20] In this case the two $d\sigma^*$ electrons are removed, the system now having d^7-d^7 configuration. There is formation of a single metal–metal bond and a consequent shortening of the metal–metal distance. In Table II is reported a comparison of geometric properties of several metal dithiocarboxylato derivatives having different configuration. What immediately transpires is the correlation between the bond order and the bond distances. It should be emphasized here that the type of ligand and the ionic radius of the metal ion are constant. Using the Pauling equation[21]:

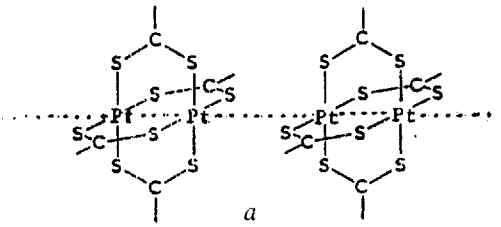
$$D_n = D_1 - a \log n'$$

where n' is defined as the bond order ($n' > 0$ and D_1 is the expected single metal–metal bond distance, it is possible to predict the metal–metal distance in the Mo derivatives. From these results it is clear that a short metal–metal distance does not necessarily imply a direct metal–metal bond. Within this scheme, a d^8-d^8 system should not have a metal–metal bond (formal bond order of zero), but a net bonding effect has been suggested by assuming an admixture of the Pt–Pt vacant $p\sigma$ or $p\sigma^*$ orbital into the occupied $d\sigma$ or $d\sigma^*$ of the neighboring atom, in such a way as to reduce the net Pt–Pt antibonding between them.[22] In conclusion, the observed geometry in tetrakis(dithiocarboxylato)dimetal(II) depends on a combination of the electronic and steric effects of the ligand and of course on the degree of metal–metal bond.

One-dimensional $Pt_2(RCS_2)_4$ chain

Binuclear Pt_2L_4 complexes contain platinum atoms of formal oxidation state +2. These binuclear chains are closely related to mononuclear platinum analogue $[Pt(CN)_4]^{2-}$ chains,[23] where the

monomer is replaced by a dimer. So, an approximate band structure of *a*



a

without calculation can be predicted using general principles of band theory beginning with the dimer as a starting unit, on the basis of what has been done previously for the linear chain $K_2Pt(CN)_4$.[24,25] The bands will arise from $d\sigma$ and $d\sigma^*$, largely made up of bonding combination φ_+ and the other from the antibonding combination φ_- of the two d_{z^2} orbitals in the dimeric unit, will be wide. In the same way the lowest unoccupied orbital $p\sigma$ ($6p_z$ in origin) will generate an empty $p\sigma$ band (conduction band). With two electrons in the $d\sigma^*$ orbital, the band formed by overlap of $d\sigma^*$ with its neighbors is full (valence band). The system therefore should be an insulator, with an energy band gap E_g. One now might wonder why $Pt_2(RCS_2)_2$ chains arrange themselves in a stacked fashion in the first place. Part of the answer has been given prevously with reference to the formation of the dimer. The invoked *p-d* mixing results in the expansion of lobes of both high-lying occupied $d\sigma^*$ and low-lying *p* orbitals outward from the intramolecular Pt–Pt bonding of adjacent units. This is favorable to interdimeric metal–metal interactions.

Optical Properties

Single-crystal absorption spectra of extremely thin crystals of $Pt_2(Pr^i\text{-}CS_2)_4$ form A and B, and of $Pt_2(CH_3CS_2)_4$ are reported in Figs. 4, 5, 6 and in Table III. For completeness the solution and solid-state diffuse reflectance spectra of these compounds is also reported.[10] The most important observation to be made is that high-intensity absorption dominates the visible region, with complete polarization of the absorption bands below 20,000 cm^{-1} along the stacking direction. The solid-state spectra above 20,000 cm^{-1} are quite similar to the solution spectra and are independent of

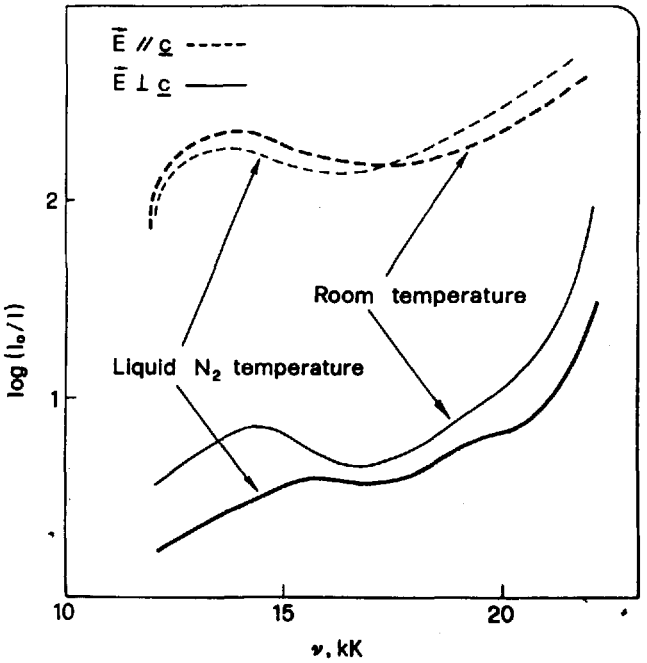


FIGURE 4 Polarized absorption spectra of $Pt_2(CH_3CS_2)_4$ at (a) 295 K and (b) 77 K. (From Ref. 10, reproduced by permission.)

the type of substituent R, being single-molecule electronic transitions, associated with metal-to-ligand charge-transfer. In the case of $Pd_2(CH_3CS_2)_4 \cdot CS_2$, the absorption band polarized along the stacking direction appears at 16,300 cm^{-1}. In $Ni_2(C_6H_5CH_2CS_2)_4$ no absorptions are observed below 19,000 cm^{-1}. How can we interpret these data, at least qualitatively? Similar optical behavior has been observed previously in the case of unoxidized tetracyanoplatinate.[26] Two models have been proposed to interpret their optical properties. The first one is based on MO tight-binding band calculations.[24,25] Following this model it has been found that the band gap energies decrease according to a R^{-3} law, where R here is the interdimeric distance, with decreasing R and that the energy bands which determine the optical and electrical properties for polarization along the stacking direction originate from Pt $5d_{z^2}$,$6s$ and Pt $6p_z$,CNπ^* hybrid

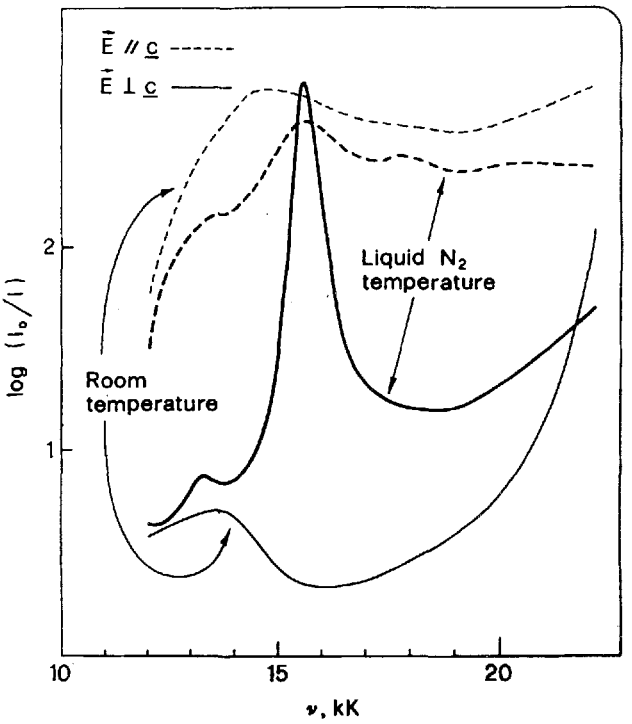


FIGURE 5 Polarized absorption spectra of $Pt_2(Pr^i\text{-}CS_2)_4$, form A, at (a) 295 K and (b) at 77 K. (From Ref. 10, reproduced by permission).

molecular states. The second one, proposed by P. Day, is based on an exciton model and assigns the lowest-energy allowed transitions as neutral Frenkel excitons formed from single-molecular transitions coupled by the intermolecular potential.[27] In both models a linearity of the R^{-3} plot was observed. In our case, due to difficulty in assigning the single-molecule *d-p* transition, only a qualitative trend of the shift of the lowest energy band as a function of the intradimeric R distance is observed. Therefore the lowest energy band, polarized along the chain direction, at 14,800 cm^{-1} (1.83 eV) could be assigned as $d\sigma^*(1a_{2u}) \rightarrow p\sigma(2a_1g)$ or π_L (L = ligand) interband transition. Perpendicular to the stacking, the observed absorption bands can be assigned as spin-forbidden transitions to triplet states. The electrical conductivity observed in the strictly columnar Pt derivatives suggests that this

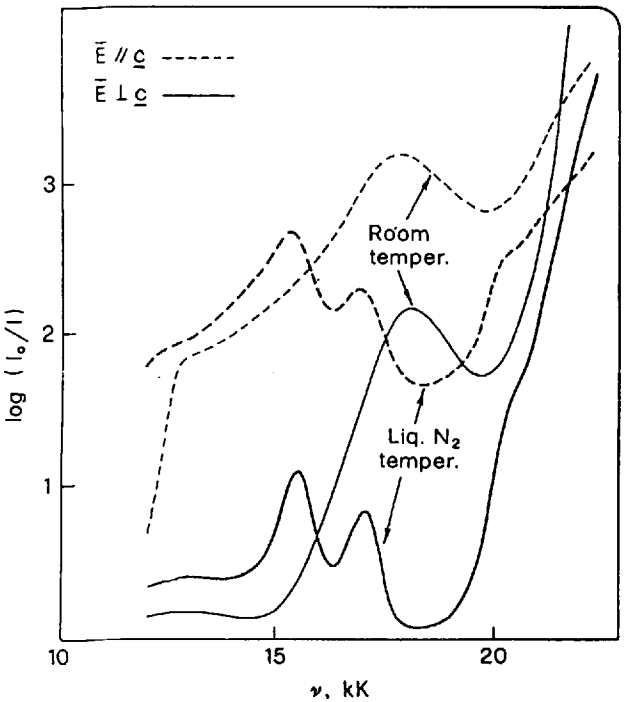


FIGURE 6 Polarized absorption spectra of $Pt_2(Pr^i\text{-}CS_2)_4$, form B, (a) at 295 K and (b) at 77 K. (From Ref. 10, reproduced by permission.)

property arises extrinsically owing to the presence of Pt^{+3} impurities, which act as acceptors for electrons to be promoted from the top of the σ^* valence band. The increase of the conductivity with decrease in Pt–Pt distance is related to an increase of the mobility of the carriers.

MIXED-VALENCE COMPOUNDS

The compounds described here clearly fulfill one of the required conditions for obtaining an inorganic electrical conductor or semiconductor, i.e., to maximize the probability of strong band formation from steric considerations. A molecular repeat unit must

TABLE III

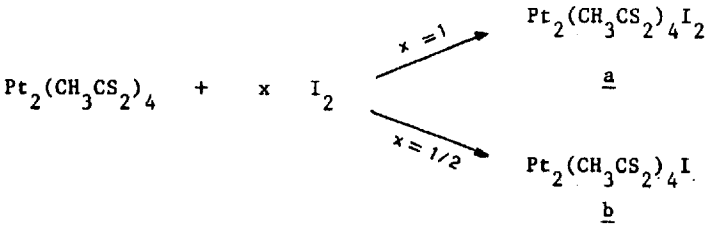
Electronic spectra (10^3 cm^{-1}) of tetrakis(dithiocarboxylato)diplatinum(II) complexes[a]

Compound	Diffuse Reflectance	Single-Crystal Absorption (r.t.) $E\|\|c$	$E\perp c$	Solution[b]	Ref.
$Pt_2(Pr^i\text{-}CS_2)_4$, form A	11.20[c]	11		20.4(2.4)	10
	14.80	14.8		24.8(3.24)	
	18.50	18.5		28.6[c](3.40)	
	23.50	n.m.		32.8(4.30)	
	n.m.			35.2[c](4.20)	
$Pt_2(Pr^i\text{-}CS_2)_4$, form B	15.0[c]	15.0	18.2		10
	18.8	18.2	n.m.		
	23.5	n.m.			
	n.m.				
$Pt_2(C_6H_5CH_2CS_2)_4$	12.8[c]	12.5		24.4[c]	10
	15.3	15.3		27.8[c]	
	23.8	23.8	23.8	32.0	
	n.m.	n.m.	n.m.		
$Pt_2(CH_3CS_2)_4$	15.2	15.2		22.8[c](2.9)	10
	19.0	19.0		24.6(3.1)	
	22.7	22.7		28.9[c](3.2)	
	24.4	n.m.		32.8(4.2)	
	n.m.			34.5[c](4.1)	

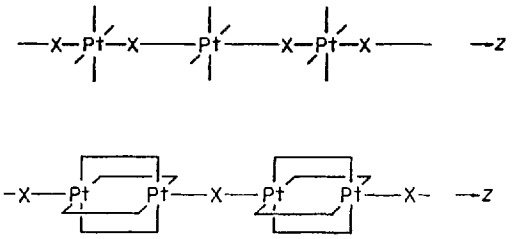
[a]n.m. = not measured beyond highest wavenumber indicated.
[b]Dichloromethane or toluene; values in parentheses as $\log(\epsilon/dm^3\ mole^{-1}\ cm^{-1})$.
[c]Shoulder.
[d]Unknown concentration due to the very low solubility.

be able to stack in such a way that close approach is permitted, as do the square planar M(II) dithiocarboxylato complexes. It was therefore straightforward to see the effect of the oxidation on these materials in the attempt to obtain a mixed-valence oxidation state. This property, also called partial oxidation or incomplete charge-transfer, greatly reduces the inhibition to charge mobility by one-site electron–electron repulsion. This means that the compounds must contain metal ions in different oxidation states, but in very similar or identical site geometries. The easiest reaction to try was the reaction with halogens.

Tetrakis(dithioacetato)diplatinum(II) readily undergoes oxidative addition with iodine to give two different products[28]:



The compound *a* is a single-valence dimeric Pt(III) complex. The compound *b* turns out to be a halogen-bridged mixed-valence Pt compound, with the formal oxidation state +2.5. The crystal structure is reported in Fig. 7 and consists of $-[Pt_2S_8]-I-[Pt_2S_8]-I-$. The compound is characterized by having a shorter Pt–Pt distance compared to the unoxidized compound, i.e., 0.1 Å. The metal–iodine–metal bridge is nearly symmetric and all the platinum and iodine atoms lie perfectly on the two-fold axes of the unit-cell. Similar reactions have been carried out for $Ni_2(CH_3CS_2)_4$ and for the $Pd_2(CH_3CS_2)_4$. Only in the case of nickel has it been possible to isolate a crystalline product, having formula $Ni_2(CH_3CS_2)_4I$.[14] The crystal structure is quite similar to that found for the Pt analogue, except for the intra- and intermolecular distances (see Table IV). Thus, these compounds belong to the class of singly bridged mixed-valence compounds, the most famous and classic compound of which is represented by Wollfram's red salt: $[Pt(C_2H_5NH_2)_4]\ [Pt(C_2H_5NH_2)_4Cl_2]$[29] (see Scheme III):



SCHEME III

The physical properties shown by these compounds are quite interesting. First of all, they are semiconductors, and the electrical

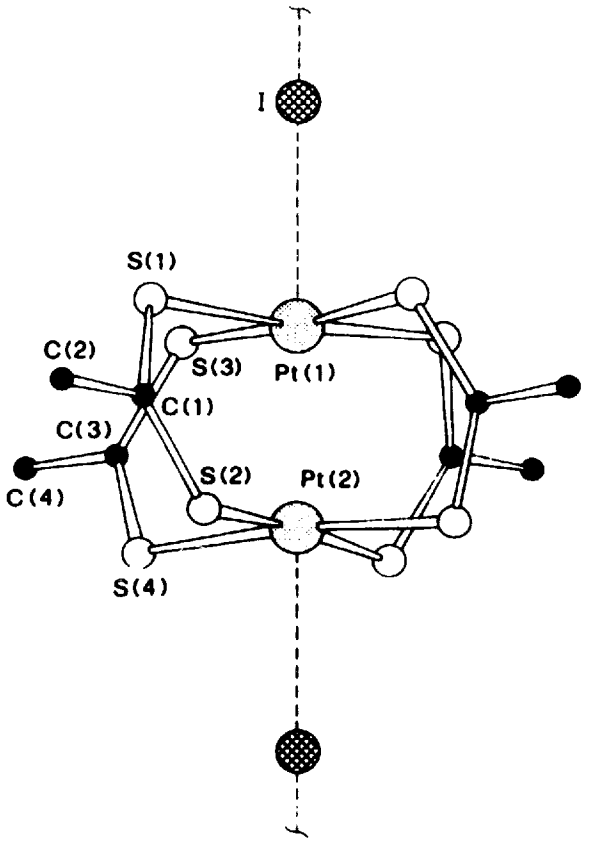


FIGURE 7 Atomic arrangement of $Pt_2(CH_3CS_2)_4I$ along the $\bar{2}$ axis. (After Ref. 28, reproduced by permission.)

conductivity at r.t. is quite high compared with that of the other compounds of this class. Each of them shows an asymmetric broad electronic band in the near infrared region, at 6,000 cm^{-1} for $Ni_2(CH_3CS_2)_4I$ and at 7,800 cm^{-1} for $Pt_2(CH_3CS_2)_4I$, absent in the starting materials. Both compounds are diamagnetic and XPS studies suggest only one type of oxidation state is present, intermediate between oxidation state II and III. The nickel derivative represents, together with catena (μ-bromo)bis((1R,2R)-cyclohexanediamine)nickel bromide,[30] the only example where singly bridged

TABLE IV

Selected bond distances (Å) for $M_2(CH_3CS_2)_4I$

Compound	M–M	M(1)–I	M(2)–I
$Ni_2(CH_3CS_2)_4I$	2.514(5)	2.928(4)	2.940(4)
$Pt_2(CH_3CS_2)_4I$	2.677(2)	2.981(3)	2.975(3)

1D mixed-valence Ni ions are present. A recent tight-binding band structure calculation, based upon extended Hückel method, has been performed by Whangbo and Canadell on binuclear platinum chains $[Pt_2(L\text{-}L)_4X]^{n-}$, where L-L = HCS_2^-, X = I, n = 0 and L-L = $(HO_2\text{–}P\text{–}O\text{–}PO_2H)^{2-}$, X = Br, n = 4, in an attempt to explain their properties.[31] Mononuclear chains $[Pt^{4+}L_4X_2 \cdot Pt^{2+}L_4]_\infty$, L = $C_2H_5NH_2$, do not adopt a symmetrical $Pt^{3+}\text{–}X\text{–}Pt^{3+}$–, but an asymmetrical $Pt^{4+}\text{–}X \cdots Pt^{2+} \cdots$ bridge. The d_{z^2} band of Pt^{3+}–X–Pt^{3+} system is half-filled, since each site contributes one electron to the band. Thus, the distortion of the bridge is a consequence of the Peierls instability, associated with a half-filled band.[32] In our system, each $Pt_2(L\text{-}L)_4$ unit contributes three electrons to the two σ and σ^* bands and therefore the higher-lying one becomes half-filled (see Fig. 8). By analogy with the mononuclear platinum chains, it would be expected that the binuclear Pt chain also undergoes a Peierls distortion of the type:

$$\cdots \overset{2.5+}{\text{X–Pt–}}\overset{2.5+}{\text{Pt–X–}}\overset{2.5+}{\text{Pt–}}\overset{2.5+}{\text{Pt–X–}}\overset{2.5+}{\text{Pt–}} \cdots$$

$$\downarrow \text{ distortion}$$

$$\cdots \overset{3+}{\text{X–Pt–}}\overset{3+}{\text{Pt–X}} \cdots \overset{2+}{\text{Pt–}}\overset{2+}{\text{Pt}} \cdots \overset{3+}{\text{X–Pt–}} \cdots$$

but the distortion is not observed experimentally at r.t. The model suggests a low-spin metallic state for symmetrical $\cdots Pt^{2.5+}\text{–}Pt^{2.5+}\text{–}X\text{–}Pt^{2.5+}\cdots$. On the other hand, the compounds are semiconductors with an activation energy which is two orders of magnitude smaller than the reflectance peak, therefore excluding a

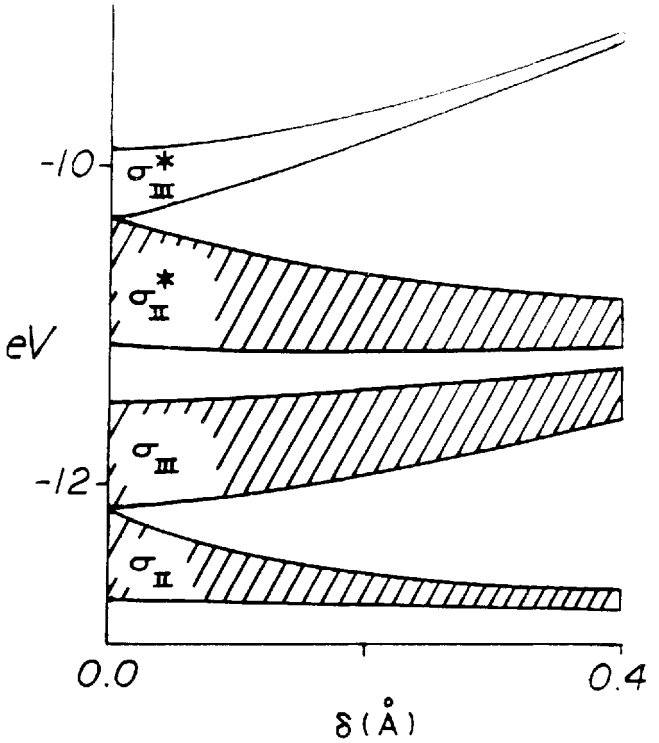


FIGURE 8 Widths of σ (d_z2 in origin) bands of binuclear Pt chain $[Pt_2(HCS_2)_4I]_\infty$ as a function of distortion of bridging halides. The shaded area indicates that each band orbital is doubly occupied. This is under the assumption of the fact that the system adopt low-spin states. (After Ref. 31, reproduced by permission.)

conduction band mechanism.[33] An alternative picture which can avoid the above problem is the localized electronic state. Consistent with this localized picture is the suggested hopping mechanism for the electrical conductivity and the strong peak in the reflectance spectrum. Nevertheless, unsatisfactory aspects, such as the magnetic behavior, still exist.[28,34] From the experimental point of view, it is important to note that linear chain compounds have been isolated only in the case of dithioacetato derivatives. The oxidative addition of iodine to Pt(II) dithiocarboxylato derivatives studied always gives Pt(III) dinuclear molecules of general formula

$Pt_2(RCS_2)_4I_2$. Why is this so? The answer may lie in the fact that in the latter a single metal–metal bond is formed since electrons are being removed from the σ^* antibonding orbital.

Acknowledgments

The work described here has been done with my colleagues, whose names appear in the references. This research is part of the research program on "Low-Dimensional Inorganic Compounds," which is supported by the Consiglio Nazionale delle Ricerche.

References

1. See, for example: *Extended Linear-Chain Compounds*, Vols. I, II, III, ed. J. S. Miller (Plenum Press, 1983).
2. S. Yoshimura, in *Molecular Metals*, ed. W. E. Hatfield, NATO Conf. Series VI: Mater. Science. (1979), p. 471.
3. *Organic and Inorganic Low-Dimensional Materials*, ed. P. Delhaes, NATO ASI Series B**168** (Plenum Press, 1987).
4. S. Scheithauser and R. Mayer, *Thio- and Dithiocarboxylic Acids and Their Derivatives*, in Topics in Sulphur Chemistry Vol. IV, (G. Thieme Pu., Stuttgart, 1979).
5. M. Bonamico, G. Dessy, V. Fares and L. Scaramuzza, J. Chem. Soc., Dalton Trans. 2250 (1975).
6. P. Day, in *The Physics and Chemistry of Low-Dimensional Solids*, ed. Luis Alcacer, NATO ASI Series C, **56** (1980), 305.
7. C. Bellitto, G. Dessy, V. Fares and A. Flamini, J. Chem. Soc., Chem. Comm. 409 (1981).
8. C. Bellitto, A. Flamini, O. Piovesana and F. Zanazzi, Inorg. Chem., **18**, 2258 (1979).
9. C. Furlani, A. Flamini, A. Sgamellotti, C. Bellitto and O. Piovesana, J. Chem. Soc., Dalton Trans. 2404 (1973).
10. C. Bellitto, M. Bonamico, G. Dessy, V. Fares and A. Flamini, J. Chem. Soc., Dalton Trans. 35 (1987).
11. T. Kawamura, T. Ogawa, T. Yamabe, H. Masuda and T. Taga, Inorg. Chem. **26**, 3547 (1987).
12. C. Bellitto, A. Flamini, O. Piovesana and P. F. Zanazzi, Inorg. Chem. **19**, 3632 (1980).
13. M. Bonamico, G. Dessy and V. Fares, J. Chem. Soc., Dalton Trans. 2315 (1977).
14. C. Bellitto, G. Dessy and V. Fares, Inorg. Chem. **24**, 2815 (1985).
15. M. A. Filomena Dos Remedios Pinto, P. J. Sadler, S. Neidle, M. R. Sanderson, A. Subbiah and R. Kuroda, J. Chem. Soc., Chem. Comm. 13 (1980).
16. L. S. Hollis and D. J. Lippard, J. Amer. Chem. Soc. **103**, 1230 (1981).
17. J. M. Burke and J. P. Fackler, Inorg. Chem. **11**, 3000 (1972).

18. G. Ciullo and O. Piovesana, Inorg. Chem. **19**, 2871 (1980).
19. K. R. Mann, J. G. Gordon and H. B. Gray, J. Amer. Chem. Soc., **97**, 3553 (1975).
20. C. Bellitto, M. Bonamico, G. Dessy, V. Fares and A. Flamini, J. Chem. Soc., Dalton Trans. 595 (1986).
21. L. Pauling, *The Nature of the Chemical Bond and the Structure of Molecules and Crystals* (Cornell University Press, Ithaca, N.Y., 1960).
22. G. G. Christoph and Y. B. Koh, J. Amer. Chem. Soc. **101**, 1422 (1979).
23. J. M. Williams, A. J. Schultz, A. E. Underhill and K. Carneiro, in Ref. 1, Vol. 1, p. 73.
24. M. H. Whangbo and R. Hoffman, J. Amer. Chem. Soc. **100**, 6093 (1978).
25. H. Yersin, G. Gliemann and U. Rössler, Solid State Comm. **21**, 915 (1977).
26. H. Yersin and G. Gliemann, Structure and Bonding **62**, 89 (1985).
27. P. Day, J. Amer. Chem. Soc. **97**, 1588 (1975).
28. C. Bellitto, A. Flamini, L. Gastaldi and L. Scaramuzza, Inorg. Chem. **22**, 444 (1983).
29. H. H. Keller, in Ref. 1, Vol. 1, p. 357.
30. H. Toftlund and O. Simonsen, Inorg. Chem. **23**, 4261 (1984).
31. M. H. Whangbo and E. Canadell, Inorg. Chem. **25**, 1726 (1986).
32. M. H. Whangbo and M. J. Foshee, Inorg. Chem. **20**, 113 (1981).
33. J. S. Miller and A. Epstein, Prog. Inorg. Chem. **20**, 1 (1976).
34. L. G. Butler, M. H. Zietlow, C. M. Che, W. P. Schaefer, S. Sridhar, P. J. Gunthaner, B. I. Swanson, R. J. H. Clark and H. B. Gray, J. Amer. Chem. Soc. **110**, 1155 (1988).
35. F. A. Cotton, P. E. Fauwick, R. H. Niswander and J. W. Setukoski, Acta Chem. Scand., Ser. A **32**, 663 (1978).