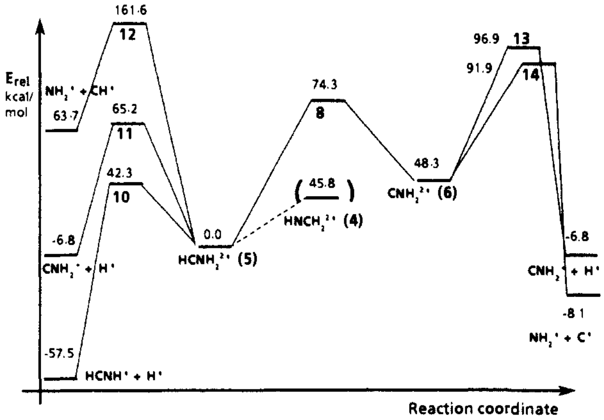

Figure 1. Potential energy diagramme for CH_3N^{2+} isomers. Relative energies (referred to the energy of H_2NCH^{2+} (*5*)) are given in kcal/mol. The reaction co-ordinate is a complex co-ordinate.

transition state of singlet diradicaloid character. As the UHF method (which has been used to localize this saddle point) is known for its poor description of singlet diradicals, the energy of TS14 is likely to be too high. But, ion **6** also seems to be prevented by significant barriers from spontaneous dissociation. In Figure 1 the various isomerization/dissociation processes are given in a simplified two-dimensional potential energy surface.

Heats of formation $\Delta H_f°$, of **5** and **6** can be estimated from combining the $\Delta H°_r$ of reactions 1–5 with the experimentally determined heats of formation of the various mono-cations;[14] by doing this, for H_2NCH^{2+} (**5**) an averaged value of $\Delta H_f° = 644$ kcal/mol and for H_3NC^{2+} (**6**) of $\Delta H_f° = 700$ kcal/mol is obtained. Both numbers indicate the extreme thermodynamic instability of the two dications, and it is highly unlikely to ever generate a stable CH_3N^{2+} species in solution. Proton transfer to the solvent shell or capture of negatively charged species from it will occur with avidity.

Acknowledgment. The financial support of our work by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie is gratefully acknowledged. We are particularly indebted to the Computer Centres of TU Berlin and the Konrad-Zuse-Zentrum Berlin for generously providing computer time.

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(14) Rosenstock, H. M.; Draxl, K.; Steiner, B. W.; Herron, J. T. *J. Phys. Chem. Ref. Data*, **1977**, 6.

Nonempirical Valence Bond Studies of the Origin of the Antiferromagnetism of Copper(II) Carboxylate Dimers

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Abstract: The origin of the antiferromagnetism of copper(II) carboxylate dimers is examined by using nonempirical valence bond procedures to calculate values for $-2J = E_{triplet} - E_{singlet}$, in which J is the magnetic exchange parameter. Ten electrons and six atomic orbitals are explicitly included in the calculations. The orbitals consist of the copper $d_{x^2-y^2}$ and a lone-pair $2p\bar{\pi}$ orbital on each oxygen atom of two carboxylate ligands. The nearest-neighbor Cu–O overlap is essentially σ in character. The results of the calculations support a conclusion obtained from an earlier semiempirical study, namely that O–O overlap within each of the carboxylate ligands is primarily responsible for the antiferromagnetism. The O–O overlap becomes effective when the oxygen lone-pair electrons delocalize into the singly occupied $d_{x^2-y^2}$ orbitals and leads to appreciable stabilization of the $S = 0$ state via covalent–ionic resonance. For $-2J \simeq 300$ cm^{-1}, the primary covalent and ionic structures for this purpose involve three $2p\bar{\pi}$-electrons within either or both carboxylate ligands. The resulting covalent–ionic resonance leads to the development of a Pauling "3-electron bond", O•••O(≡O: •O ↔ O• :O) within a carboxylate ligand.

The copper acetate monohydrate dimer is perhaps the best-known member of a large class of similarly structured Cu(II) carboxylate dimers with the general formula $Cu_2(RCO_2)_4L_n$, where $n = 0$ or 2. Each of these dimers involves two Cu^{2+} ions which are bridged symmetrically by four carboxylate ligands. It is well-known that this type of dimer involves an $S = 0$ ground state, i.e., the spins of the two magnetic electrons which originate from the $(3d)^9$ configurations of the two Cu^{2+} ions are antiparallel, and a thermally accessible $S = 1$ excited state. As a result, antiferromagnetism is observed. A singlet–triplet energy separation ($^3E - {}^1E = -2J$) of 286 cm^{-1} has been reported[1,2] for $Cu_2(CH_3CO_2)_4$, $2H_2O$, and other copper(II) carboxylate dimers have $-2J$ values of 100–550 cm^{-1}.[3-7]

To account for the antiferromagnetism of copper acetate, Figgis and Martin[1,2] suggested that for the $S = 0$ ground state, a weak Cu–Cu δ-bond is formed by the lateral overlap of singly occupied $3d_{x^2-y^2}$ atomic orbitals (AOs). For this type of bond, Ross and

Table I. Atomic Orbital Overlap Integrals

S_{12}	0.069 41 (0.069 2)[a]	S_{15}	0.000 07 (0.0)[a]
S_{13}	0.000 38 (0.000 29)[a]	S_{16}	0.000 38 (0.000 53)[a]
S_{14}	0.019 60 (0.011 27)[a]	S_{23}	0.001 09 (0.000 23)[a]

[a] Reference 15, with sp^2 hybridized oxygen AOs, $\zeta_O = 2.2266$ and $\zeta_{Cu}(3d) = 3.080$.

[†] University of Melbourne.

[‡] University of Canterbury.

(1) Figgis, B. N.; Martin, R. L. *J. Chem. Soc.* **1956**, 3837.

(2) Martin, R. L. In *New Pathways in Inorganic Chemistry*; Ebsworth, E. A. V.; Maddock, A. G., Sharpe, A. G., Eds.; Cambridge University Press: London, 1968; p 175.

(3) Jotham, R. W.; Kettle, S. F. A.; Marks, J. A. *J. Chem. Soc. Dalton Trans.* **1972**, 428.

(4) Doedens, R. J. *Prog. Inorg. Chem.* **1976**, *21*, 209.

(5) Catterick, J.; Thornton, P. *Adv. Inorg. Radiochem.* **1977**, *20*, 291.

(6) Melnik, M. *Coord. Chem. Rev.* **1981**, *36*, 1; **1982**, *42*, 259.

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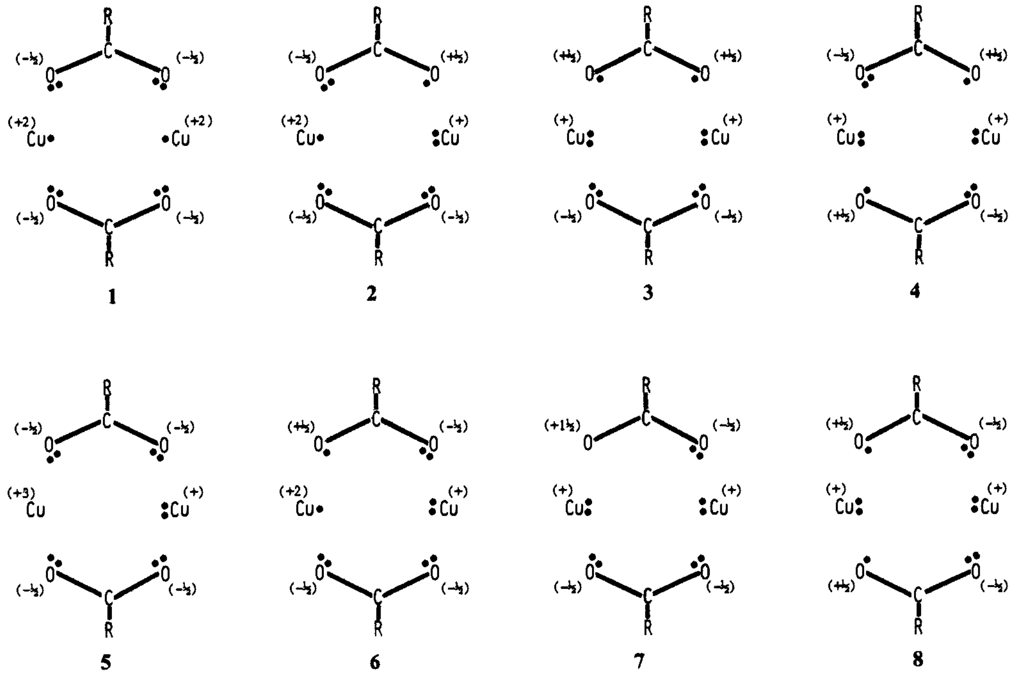
Chart I



Yates[8] calculated a value of 4 cm^{-1} for $-2J$ using valence bond (VB) procedures. The VB structures that were included in the treatment were Cu↑ ↓Cu, Cu$^{(-)}$ Cu$^{(+)}$, and Cu$^{(+)}$ Cu$^{(-)}$ for the $S = 0$ state and Cu↑ ↑Cu for the $S = 1$ state. Thus according to this calculation, the Cu–Cu δ-bond has insufficient strength to account for the observed magnitude for $-2J$. On the other hand, a $-2J$ value of 1600 cm^{-1}, which has been calculated[8] for a Cu–Cu σ-bond (with the same types of VB structures), indicates that a Cu–Cu σ-bond is too strong.

Bleaney and Bowers[9] recognized that orbitals and electrons from the acetate ligands should also be involved in the explanation of the origin of the antiferromagnetism. A number of calculations have been reported which take these orbitals into account.[10-18] (Some of them have been reviewed in ref 15 and 18.) From a VB point of view, the primary orbitals for this purpose are the oxygen lone-pair orbitals that can overlap with the $d_{x^2-y^2}$ orbitals of the Cu^{2+} ions.[12,15,19-21] These orbitals are displayed in Figure 1 for two carboxylate ligands, in which the Cu–O overlap is essentially σ in character. (Gerloch and Harding[16] have involved Cu–O π-bonding via d_{xy}–$p\pi$ overlap and $d_{x^2-y^2}$–d_{xy} configurational mixing.) The oxygen lone-pair electrons can delocalize into the singly occupied $d_{x^2-y^2}$ orbitals, thereby giving rise to a superexchange mechanism for the spin-pairing. When this delocalization occurs, the overlap between the oxygen orbitals of each carboxylate ligand becomes effective for helping to stabilize the $S = 0$ state relative to the $S = 1$ state.[14,15] If the oxygen orbitals are $\bar{\pi}$ AOs, as they are for the free ligand,[22] the O–O overlap integral has a value of 0.0196 (Table I).

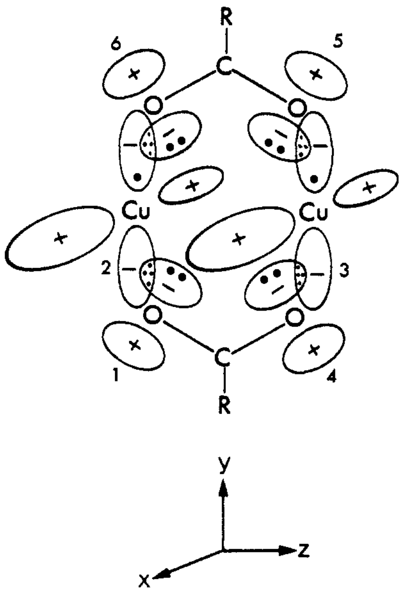


Figure 1. Copper $3d_{x^2-y^2}$ and oxygen $2p\bar{\pi}$ atomic orbitals.

The results of some semiempirical molecular orbital (MO) studies for this superexchange model have been reported previously.[15] Ten AOs and 18 electrons were included in one of the calculations, which involved configuration interaction (CI) for twelve $^1A_{1g}$ and seven $^3A_{2u}$ configurations (D_{4h} symmetry was assumed). With a value of 0.011 for the O–O overlap integral, a value of 260 cm^{-1} was calculated for $-2J$. A smaller calculation,

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(7) Mehrotra, R. C.; Bohra, R. *Metal Carboxylates*; Academic Press: London, 1983; p 61.

(8) Ross, I. G.; Yates, J. *Trans. Faraday Soc.* **1959**, *55*, 1064.

(9) Bleaney, B.; Bowers, K. D. *Proc. R. Soc. London* **1952**, *A214*, 451.

(10) Muto, Y.; Kato, M.; Jonassen, H. B.; Cusachs, L. C. *Bull. Chem. Soc. Jpn.* **1969**, *42*, 417.

(11) Bersuker, I. B.; Titova, Yu. G. *Theor. Expt. Chem.* **1970**, *6*, 381.

(12) Harcourt, R. D. *Aust. J. Chem.* **1974**, *27*, 2065.

(13) Hay, P. J.; Thibeault, J. C.; Hoffmann, R. *J. Am. Chem. Soc.* **1975**, *97*, 4804.

(14) Kahn, O.; Briat, B. *J. Chem. Soc., Faraday Trans. 2* **1976**, *72*, 268.

(15) Harcourt, R. D.; Martin, G. E. *J. Chem. Soc., Faraday Trans. 2* **1977**, *73*, 1.

(16) Gerloch, M.; Harding, J. H. *Proc. R. Soc. London* **1978**, *A360*, 211.

(17) Kawamori, A. *J. Magn. Res.* **1978**, *31*, 423.

(18) de Loth, P.; Cassoux, P.; Daudey, J. P.; Malrieu, J. P. *J. Am. Chem. Soc.* **1981**, *103*, 4007. See also: de Loth, P.; Daudey, J. P.; Astheimer, H.; Walz, L.; Haase, W. *J. Chem. Phys.* **1985**, *82*, 5048 and references therein.

(19) Harcourt, R. D. In *Methods and Structure of Quantum Science*; Calais, J.-L., Goscinski, O., Linderberg, J., Öhrn, Y., Eds.; Plenum: New York, 1976; p 105. A list of typographical errata for this paper, and for ref 21 below, may be obtained from the author.

(20) Harcourt, R. D. *J. Am. Chem. Soc.* **1980**, *102*, 5195; **1981**, *103*, 5623.

(21) Harcourt, R. D. *Lecture Notes in Chemistry*; Springer: Heidelberg, 1982; Volume 30, Chapter 8.

(22) The $2p\bar{\pi}$ AOs are oriented perpendicular to the C–O bond axes, but with their axes lying in the CO$_2^-$ plane. The $2s_O$ electrons are more firmly bound, and therefore they will have a smaller tendency to delocalize. Therefore these electrons have been assumed to be localized in the present treatment. In the complex, the $2p\bar{\pi}$ and 2s AOs will hybridize to some extent; the optimum hybridization would need to be ascertained by calculation.

Table II. Singlet-Triplet Energy Separations ($-2J$/cm^{-1}) for Two Carboxylate Ligands + Two Cu^{2+} ions[a]

(Z_{Cu}, Z_O)	all structures	all covalent structures	**1** ↔ **5** + **3** ↔ **7**	**2** ↔ **6** + **4** ↔ **8**	omit **2** ↔ 6	omit 4 ↔ **8**
(3,1.5)	183 (1.21×10^5)	16	12	3.54×10^3	14	127
(2,1.5)	35 (2.55×10^5)	4	15	2.29×10^3	15	34
(1,1.5)	25 (3.93×10^5)	3	19	2.02×10^3	19	25
(3,1)	1.44×10^3 (5.84×10^4)	94	25	7.45×10^3	183	583
(2,1)	78 (1.82×10^5)	8	15	3.02×10^3	15	68
(1,1)	32 (3.18×10^5)	4	18	2.38×10^3	18	32
(3,0.5)	7.62×10^3 (2.05×10^4)	404	3.55×10^3	1.52×10^4 (4.15×10^3)	1.97×10^4 (1.80×10^3)	2.16×10^3
(2,0.5)	332 (1.12×10^5)	26	16	4.74×10^3	20	213
(1,0.5)	52 (2.44×10^5)	6	18	2.91×10^3	18	49

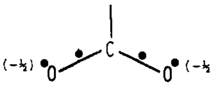
[a] Values in parentheses refer to the $S = 1$ state with B_{2u} symmetry.

with two instead of four carboxylate ligands, eight ^1A_g, and six $^3B_{1u}$ configurations, gave $-2J = 780$ cm^{-1}. When the O–O overlap integral was omitted from the latter calculation, the value for $-2J$ was reduced to ~0 cm^{-1}. Therefore, according to these studies, O–O overlap within each carboxylate ligand, rather than Cu–Cu overlap, is primarily responsible for the antiferromagnetism.

The purpose of the present paper is to provide further support for the O–O overlap hypothesis by means of a series of nonempirical VB calculations for the ten electrons and six AOs of Figure 1. A similar type of semiempirical VB study has been reported previously in ref 15. For both studies, the size of the VB calculations restricted us to a consideration of the D_{2h} (10 electrons, 6 AOs) rather then the D_{4h} (18 electrons, 10 AOs) model. However, for comparison, we also report the results of nonempirical calculations for two Cu^{2+} and one carboxylate ligand (i.e., 6 electrons and 4 AOs). The general conclusions concerning the origin of the antiferromagnetism that are obtained from the two sets of calculations are not expected to change for a D_{4h} treatment.

Lewis Valence-Bond Structures

There are 21 $S = 0$ and 15 $S = 1$ Lewis-type VB structures for the 10-electron 6-orbital model[15,19–21]. (In each of these structures, we use an average π-electron representation, namely



for the four π-electrons of each carboxylate ligand.) The $S = 0$ structures are of types **1–8**, with antiparallel spins for the two unpaired electrons.[23] The $S = 1$ structures are of types **1–4**, **6**, and **8**, in which the unpaired electrons have parallel spins. For either spin state, structures of types **2** and **6** arise from the delocalization of one oxygen electron into a copper orbital. Ten $S = 0$ structures of types **3**, **4**, **7**, and **8** arise from the delocalization of two oxygen electrons. Two-electron delocalizations also generate six $S = 1$ structures of types **3**, **4**, and **8**. For either spin state, nine of the structures are covalent in the sense that each of the two O–Cu–O moieties has five electrons, while the remaining structures are ionic, i.e., the O–Cu–O moieties involve either four or six electrons. A similar classification of VB structures has now been used on numerous occasions to help describe the origin of the long N–N and S–S bonds of N_2O_4 and $S_2O_4^{2-}$, and the "cis O–O overlap" contribution to the rotation barrier of N_2O_4.[20,24]

The VB analysis of the MO-CI wave functions of ref 15 indicated that pairs of equivalent $S = 0$ and 1 covalent structures with the same orbital occupancies were degenerate when zero differential overlap was assumed. This degeneracy is removed in the nonempirical VB studies of the present paper. For both sets of calculations, the stabilization of the $S = 0$ state relative to the $S = 1$ state arises either entirely[15] or primarily from resonance between covalent and ionic VB structures. For the two spin states, the following types of covalent-ionic resonance need to be considered:

$$S = 0:\ \mathbf{1} \leftrightarrow \mathbf{5};\ \mathbf{2} \leftrightarrow \mathbf{6};\ \mathbf{3} \leftrightarrow \mathbf{7};\ \mathbf{4} \leftrightarrow \mathbf{8}$$

$$S = 1:\ \mathbf{2} \leftrightarrow \mathbf{6};\ \mathbf{4} \leftrightarrow \mathbf{8}$$

Except for **1** ↔ **5**, the stabilization energies that arise from each of the types of covalent-ionic resonance are either partially (**2** ↔ **6**)[25] or entirely (**3** ↔ 7 and **4** ↔ **8**) O–O overlap dependent. Which of these different types of covalent-ionic resonance is important for rationalizing the origin of the antiferromagnetism depends on the extent of delocalization of the oxygen lone-pair electrons of **1** and on the symmetry of the $S = 1$ state. For the semiempirical calculations of ref 15, the **4** ↔ **8** type resonance was identified as the primary type, but this was not considered to be a general result.[20,21] Here, without the zero differential overlap assumption, we shall show that either **2** ↔ **6** or **4** ↔ **8** is the dominant type of resonance if the extent of delocalization is either small or large.

In VB structures **1–8**, we have for clarity not indicated the presence of any Cu–O or Cu–L bonding that would arise from the utilization of the copper 4s and 4p AOs in the bonding schemes. The results of ab initio MO calculations give 4s, $4p_x$, $4p_y$, and $4p_z$ AO populations of 0.39, 0.23, 0.22, and 0.14, respectively.[18] To simplify our calculations, we have not included the 4s and 4p AOs explicitly. The effect of this type of bonding on the extent of delocalization of the oxygen electrons into the $3d_{x^2-y^2}$ AOs is simulated through the values that we have used for the core charges Z_{Cu} and Z_O.

In our VB treatment, we have assumed that the primary ligand orbitals that are involved in the superexchange mechanism are acetate lone-pair AOs. Although these orbitals will overlap with those of the C–C σ-bond of acetate, the extent of interaction must be very small, since estimates of the C–C bond lengths for the acetate ligands and CH_3—$CHCH_2$ are almost identical, cf. 1.501 Å[26,27] for both species. This type of interaction is absent in CH_3—$CHCH_2$, where no lone-pair $2p\bar{\pi}$ electrons are present. Consequently we have excluded the C–C orbitals from the calculations.

Method of Calculation

The geometry reported in ref 26a for the copper acetate monohydrate dimer was assumed for each of the $S = 0$ and 1 spin states. Slater $3d_{x^2-y^2}$ and 2p orbitals were used, with $^1/_2(Cu^{2+} + Cu^+)$ and $^1/_2(O + O^-)$ Slater orbital exponents. The oxygen lone-pair AOs were assumed to be $2p\bar{\pi}$ orbitals,[22] as in the free carboxylate ligand. The $S = 0$ bond-eigenfunctions for the VB structures **1–4**, **6**, and **8** have the general form $|Ra\bar{b}| + |Rb\bar{a}|$; those for **5** and **7** are given by $|Rc\bar{c}|$. The $S = 1$ bond-eigenfunctions for each of **1–4**, **6**, and **8** are of the $S_z = 0$ type, namely, $|Ra\bar{b}| - |Rb\bar{a}|$. In each of these wave functions, R represents four doubly occupied AOs.

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[23] For either spin state, the number of equivalent structures of a given type are the following: (**1**) 1; (**2**) 4; (**3**) 2; (**4**) 2; (**6**) 4; (**8**) 2. There are also 2 and 4 equivalent $S = 0$ structures of the types **5** and **7**.

[24] Harcourt, R. D.: (a) *Theor. Chim. Acta* **1964**, *2*, 437; **1966**, *4*, 202. (b) *Ibid.* **1966**, *6*, 131. (c) *Int. J. Quantum Chem.* **1970**, *4*, 173. (d) *J. Mol. Struct.* **1971**, *9*, 221. (e) *Aust. J. Chem.* **1978**, *31*, 1635. (f) *Ibid.* **1979**, *32*, 933. (g) *Ibid.* **1981**, *18*, 1881. (h) Reference 21, Chapter 7. See also: Harcourt, R. D.; Smith, B. J.; Marsden, C. J. *Aust. J. Chem.* **1984**, *37*, 1553.

[25] Resonance between the four covalent structures of type **2** and the four ionic structures of type **6** generates an exchange integral which is Cu–Cu as well as O–O overlap dependent.

[26] (a) Brown, G. M.; Chidambaram, R. *Acta Crystallogr.* **1973**, *B29*, 2393. (b) de Meester, P.; Fletcher, S. R.; Skapski, A. C. *J. Chem. Soc., Dalton Trans.* **1973**, 2575.

[27] Lide, D. R., Jr.; Christensen, D. *J. Chem. Phys.* **1961**, *35*, 1374.

Table III. Magnitudes of Bond-Eigenfunction Coefficients (C_i) for VB Structures of Types **1–8**, with Z_{Cu} = 3, 2, 1 and Z_O = 1.5[a]

	(Z_{Cu},Z_O)					
	(3,1.5)		(2,1.5)		(1,1.5)	
	$S = 0$	$S = 1$	$S = 0$	$S = 1$	$S = 0$	$S = 1$
C_1	0.885	0.887	0.977	0.977	0.993	0.993
C_2	0.224	0.224	0.105	0.105	0.060	0.060
C_3	0.052	0.052	0.0106	0.0106	0.003	0.003
C_4	0.059	0.059	0.0114	0.0113	0.004	0.004
C_5	0.024		0.014		0.013	
C_6	0.022	0.012	0.005	0.005	0.002	0.001
C_7	0.010		0.001		0.0002	
C_8	0.005	0.0	0.001	0.0	0.0001	0.0
normalizer	0.9508	0.9514	0.9818	0.9819	0.9940	0.9941

[a] Since the AO overlap integrals are very small (Table I), the C_i^2 for this and subsequent tables should provide a reliable qualitative guide to the relative magnitudes of the VB weights.

Table IV. Magnitudes of Bond-Eigenfunction Coefficients (C_i) for VB Structures of Types **1–8**, with Z_{Cu} = 3, 2, 1 and Z_O = 1.0

	(Z_{Cu},Z_O)					
	(3,1.0)		(2,1.0)		(1,1.0)	
	$S = 0$	$S = 1$	$S = 0$	$S = 1$	$S = 0$	$S = 1$
C_1	0.629	0.648	0.947	0.947	0.986	0.986
C_2	0.336	0.339	0.158	0.158	0.083	0.083
C_3	0.155	0.155	0.025	0.025	0.007	0.007
C_4	0.194	0.187	0.027	0.027	0.007	0.007
C_5	0.046		0.018		0.014	
C_6	0.067	0.027	0.011	0.006	0.003	0.002
C_7	0.024		0.002		0.0003	
C_8	0.066	0.0	0.003	0.0	0.005	0.0
normalizer	0.9213	0.9239	0.9678	0.9680	0.9877	0.9878

Since only ten electrons are explicitly treated in the calculations, the cores for these electrons involve the remaining electrons as well as the atomic nuclei. If each of the core electrons is assumed to provide one unit of screening to the atomic nucleus around which its AO is located, the copper and oxygen core charges Z_{Cu} and Z_O have values of 3.0 and 1.5 in each of the VB structures. The difference $Z_{Cu} - Z_O$ helps to determine the extent of delocalization of the oxygen electrons, i.e., $Z_{Cu} - Z_O$ provides a (crude) measure of the electronegativity difference that exists between these atoms. Almost certainly, Z_{Cu} = 3.0 and Z_O = 1.5 are not the optimum values for the core charges, and therefore in various calculations, we have assigned values of 3, 2, and 1 to Z_{Cu} and 0.5, 1.0, and 1.5 to Z_O. One purpose for doing this was to explore how the magnitude of $-2J$ depends on the extent of delocalization of the oxygen electrons.

The VB calculations were performed with the ab initio program described in ref 28. The integrals were calculated with the Stevens program.[29]

For each set of core charges, calculations have been performed with different numbers of structures included. In Table II, the resulting $-2J$ values are reported. The coefficients for the various types of bond-eigenfunctions are reported in Tables III–V for both spin states, when all VB structures are included in the calculations.

For any set of core charges, the overlap integrals chiefly determine the magnitude of $-2J$. Some comments on the values of these integrals for both the Cu–Cu δ-bond and the O–O overlap for a carboxylate ligand are therefore relevant here. Our estimate of 0.001 for S(Cu–Cu) is only slightly smaller than the values of either 0.002 used by Forster and Ballhausen[30] and Jotham and Kettle[31] or 0.003, which was used by Ross and Yates[8] to calculate a $-2J$ value of 4 cm^{-1}. The latter workers deduced that S(Cu–Cu) = 0.011 was required in order that $-2J$ = 286 cm^{-1}. An overlap integral of 0.01 was also used in the calculations described in refs 32 and 33. For each of these calculations, only the copper AOs were explicitly treated, i.e., no allowance was made for the effect of O–O overlap on the value of $-2J$. Therefore, the smaller values of S(Cu–Cu) are probably more appropriate. Empirical evidence also exists which suggests that Cu–Cu bonding provides very little stabilization of the $S = 0$ spin state relative to the $S = 1$ spin state.[3-7,15,21,34,35]

Table V. Magnitudes of Bond-Eigenfunction Coefficients (C_i) for VB Structures of Types **1–8**, with Z_{Cu} = 3, 2, 1 and Z_O = 0.5

	(Z_{Cu},Z_O)					
	(3,0.5)		(2,0.5)		(1,0.5)	
	$S = 0$	$S = 1$	$S = 0$	$S = 1$	$S = 0$	$S = 1$
C_1	0.221	0.267	0.851	0.854	0.971	0.971
C_2	0.273	0.315	0.250	0.250	0.119	0.119
C_3	0.254	0.297	0.067	0.066	0.014	0.014
C_4	0.412	0.420	0.076	0.075	0.015	0.015
C_5	0.045		0.031		0.017	
C_6	0.109	0.027	0.030	0.015	0.007	0.004
C_7	0.058		0.008		0.001	
C_8	0.255	0.0	0.012	0.0	0.001	0.0
normalizer	0.9278	0.9301	0.9442	0.9451	0.9781	0.9782

As was indicated previously, the oxygen AOs used in the calculations were assumed to be $2p\bar{\pi}$, as for the free carboxylate ligand. If the oxygen AOs are assumed to be sp^2 hybridized relative to the C–O bond axes, the O–O overlap integral has a value of 0.015.[22] (With sp^2 hybrid AOs directed along the Cu–O bond axes, the value of the O–O overlap integral is 0.011.[15]) Both of these values, together with 0.0196 for the $2p\bar{\pi}$ AOs, are substantially larger than the 0.001 for the Cu–Cu overlap integral, and therefore it is not surprising that O–O rather than Cu–Cu overlap is calculated to be primarily responsible for the antiferromagnetism.

Results

When all structures are included in the calculations, the $-2J$ values reported in Table II increase as the difference $\Delta Z = Z_{Cu} - Z_O$ increases. For each set of Z values, the bond-eigenfunction coefficients (Tables III–V) indicate that the weights for the ionic structures are much smaller than are those for the corresponding covalent structures. Omission of the ionic structures reduces very substantially the values for $-2J$; except for Z_{Cu} = 3 and Z_O = 0.5, the $-2J$ are then much smaller than the experimental values. Since the Cu–Cu and nonneighbor Cu–O and O–O overlap integrals are so small (Table I), the concomitant covalent bonds in the covalent $S = 0$ structures **1**, **2**, and **4** are too weak to afford much stabilization of the $S = 0$ state relative to the $S = 1$ state, without assistance from resonance with ionic structures. However, the O–O overlap within a carboxylate ligand has a somewhat larger magnitude (0.0196), and therefore the $S = 0$ structures of type **3** have rather lower energies than the corresponding $S = 1$ structures. The Table VI, values for $-2J$ are reported for the four types of covalent structures alone.

As ΔZ increases, structure **1** decreases in importance, and contributions from the remaining covalent structures increase. However, as $\Delta Z \rightarrow \infty$, the contributions from all structures approach zero except for **3**, **4**, **7**, and **8**. Inspection of Tables II–V show that the **2** $\leftrightarrow$ **6** type resonance is primarily responsible for the antiferromagnetism when the extent of delocalization is small. However, when the extent of delocalization is large, diamagnetism rather than antiferromagnetism is calculated to occur ($-2J \gg 1000$ cm^{-1}), and resonance of the type **4** $\leftrightarrow$ **8**, with some help from **3** $\leftrightarrow$ **7** is primarily responsible for this effect. For intermediate amounts of delocalization, each of **2** $\leftrightarrow$ **6**, **3** $\leftrightarrow$ **7**, and **4** $\leftrightarrow$ **8** is of importance for rationalizing the origin of the antiferromagnetism. For example, with Z_{Cu} = 2 and Z_O = 0.5, a value of 332 cm^{-1} is obtained for $-2J$, which is similar to some of the experimental estimates. This value is reduced to 20 cm^{-1} when structures of types 2 and 6 are excluded and to 213 cm^{-1} when structures of types 4 and 8 are omitted. Thus for this case, **2** $\leftrightarrow$ **6** is more important than **4** $\leftrightarrow$ **8**, but the latter type of resonance is by no means insignificant in its effect. Also, it may be noted

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(28) (a) Maclagan, R. G. A. R.; Schnuelle, G. W. *J. Chem. Phys.* **1971**, *55*, 5431. (b) Jans, R.; Maclagan, R. G. A. R. *Aust. J. Chem.* **1984**, *37*, 2159.

(29) Stevens, R. M. *J. Chem. Phys.* **1971**, *55*, 1725.

(30) Forster, L. S.; Ballhausen, C. J. *Acta Chem. Scand.* **1962**, *16*, 1385.

(31) Jotham, R. W.; Kettle, S. F. A. *Inorg. Chem.* **1970**, *9*, 1390.

(32) Dubicki, L.; Martin, R. L. *Inorg. Chem.* **1966**, *5*, 2203.

(33) Boudreaux, E. A. *Inorg. Chem.* **1964**, *3*, 506.

(34) Goodgame, D. M. L.; Hill, N. J.; Marsham, D. F.; Skapski, A. C.; Smart, M. L.; Troughton, P. G. H. *J. Chem. Soc., Chem. Commun.* **1969**, 629.

(35) Reference 21, p 91.

(36) Green, M.; Linnett, J. W. *J. Chem. Soc.* **1960**, 4959.

(37) Linnett, J. W.: (a) *J. Am. Chem. Soc.* **1961**, *83*, 2643. (b) *The Electronic Structures of Molecules*; Methuen: London 1964. (c) *Sci. Prog. Oxford* **1972**, *60*, 1.

(38) Harcourt, R. D. *J. Chem. Educ.* **1985**, *62*, 99.

Table VI. Singlet-Triplet Energy Separations ($-2J$) for Sets of Covalent and Ionic Structures[a]

covalent		covalent ↔ ionic	
	$-J/cm^{-1}$		$-2J/cm^{-1}$
1	2–3 (2–3)	**1** ↔ **5**	12–19 (12–19)
2	41–48 (42–49)	**2** ↔ **6**	1.84×10^3–2.26×10^3 (1.41×10^3–1.76×10^3)
3	592–767 (592–767)	**3** ↔ **7**	2.32×10^3–3.60×10^3 (2.32×10^3–3.60×10^3)
4	79–88 (–)	**4** ↔ **8**	1.71×10^4–2.16×10^4 (–)

[a] The value of $-2J$ for each set of structures is slightly sensitive to variation in the core charges Z_{Cu} and Z_O. Minimum and maximum values are reported for the calculations that have been performed. Values in parentheses obtain to the 6-electron 4-AO model, with one carboxylate ligand.

that the ionic structures of type **8** do not contribute to the $^3B_{1u}$ state, i.e., only the $S = 0$ form of **4** is stabilized by covalent–ionic resonance.

Inspection of Tables III–V shows that only the covalent structures of type **2** have ionic partners in the $^3B_{1u}$ state. Therefore, covalent–ionic resonance of the type **2** ↔ **6** occurs in both spin states. The coefficients for $^1\Psi_2$ and $^3\Psi_2$ are similar, whereas the coefficient for $^3\Psi_6$ is rather smaller than that for $^1\Psi_6$. Therefore, covalent–ionic resonance of the type **2** ↔ **6** stabilizes the $S = 0$ state to a rather larger extent than it does for the $S = 1$ state. The resulting values for $-2J$ (Table VI) range from 1840 to 2260 cm^{-1}. The smaller degree of covalent–ionic resonance for the $S = 1$ state is a consequence of the nonnegligible value of 0.069 for the Cu–O overlap integral which relates to the singly occupied AOs of **6**. This affects the energy separation $^3E_6 - {}^1E_6$, for which our estimates are 16800–18740 cm^{-1}. In contrast the nonneighbor Cu–O overlap integral for the singly occupied AOs of **2** is very small (0.0004), and therefore $^3\Psi_2$ and $^1\Psi_2$ lie much closer in energy. Our estimates for $^3E_2 - {}^1E_2$ are 41–48 cm^{-1}.

As indicated earlier, the O–O overlap within the carboxylate ligand is almost entirely responsible for the antiferromagnetism (via covalent–ionic resonance) if the Cu–Cu and nonneighbor Cu–O overlap integrals have very small magnitudes. Only a small degree of delocalization of oxygen lone-pair electrons is required in order that this overlap may start to stabilize the $S = 0$ state. It is of interest to note that when the $S = 0$ and 1 covalent structures of types **3** are considered alone (Table VI), $-2J$ = 590–770 cm^{-1}. These values are increased to 2300–3600 cm^{-1} when ionic structures of type **7** are included in the resonance scheme for the $S = 0$ state. These effects only become important when $Z_{Cu} - Z_O$ is very large and structures of types **4** and **8** are absent. If the latter structures are present (as occurs in the 10-electron 6-orbital calculations), they have larger weights than have **3** and **7** (Tables IV and V). This is primarily because **4** and **8** involve a more favorable spatial arrangement of net charges on the oxygen atoms than have **3** and **7**.

Reducing the values of the O–O overlap integral within a carboxylate ligand must reduce the magnitude of $-2J$. In Table VI, the $-2J$ for each of **3** ↔ **7** and **4** ↔ **8** is larger than that for **2** ↔ **6**. Therefore, if the optimum value for O–O overlap integral is smaller than the 0.0196 used in the calculations, the extent of delocalization of the oxygen lone-pair electrons must increase in order that the smaller overlap may become effective for providing an appreciable stabilization of the $S = 0$ state. This will increase the importance of **3** ↔ **7** ± **4** ↔ **8** relative to **2** ↔ **6** in rationalizing the origin of the antiferromagnetism.

The above considerations require only slight modification when superexchange via one carboxylate ligand is considered. For this case, only structures of types **1**–**3** and **5**–**7** contribute to the resonance schemes. Results of various sets of calculations are reported in Tables VI and VII. They show that for $-2J \sim 500$ cm^{-1}, resonance between structures of types **2** and **6** is primarily responsible for the antiferromagnetism. For appreciably larger values of $-2J$, the primary covalent–ionic resonance involves **3** and **7** for the $S = 0$ state. The **3** ↔ **7** resonance replaces (**3** ↔ **7** + **4** ↔ **8** for the calculations with two carboxylate ligands, for which **4** ↔ **8** is dominant, as was indicated in the previous paragraph.

When four carboxylate ligands are present, additional VB structures arise which are similar to **4** and **8**, except for the location of the unpaired electrons on oxygen atoms in adjacent rather than trans carboxylate ligands.

Table VII. Singlet–Triplet Energy Separations ($-2J/cm^{-1}$) for One Carboxylate Ligand + Two Cu^{2+} Ions

(Z_{Cu},Z_O)	all structures	**1** ↔ **2** ↔ **3**	omit **2** ↔ **6**
(3,1.5)	81	8	12
(2,1.5)	24	3	15
(1,1.5)	22	3	19
(3,1.0)	581	50	18
(2,1.0)	42	5	15
(1,1.0)	25	3	18
(3,0.5)	2.54×10^3	347	3.58×10^3
(2,0.5)	142	13	15
(1,0.5)	34	4	18

As was indicated in the Introduction, $-2J$ values of 100–550 cm^{-1} have been reported for various copper(II) carboxylate dimers[3-7] (see also ref 39 and 40). According to the theory of this paper, the variations in these values are related to differences in the electronegativities for the oxygen atoms relative to the copper atoms. These would be largely associated with the values for the oxygen core charge Z_O. When apical ligands (L) are also coordinated to the Cu^{2+} ions, the Z_{Cu} will also be affected. Geometry variations (in particular, $\angle$CuCuO) will also influence $-2J$ primarily via the Cu–O overlap. However, a correlation does not exist between the length of the Cu–Cu bond and $-2J$ (see ref 34, for example).

Elsewhere,[21,24e,g] two types of covalent–ionic resonance have been distinguished. Resonance between either **1** and **5** or **3** and **7** involves the two electrons that form the electron-pair bond in the $S = 0$ covalent structures **1** and **3**. Resonance between either **2** and **6**, or **4** and **8**, leads to the development of a Pauling "3-electron bond" (O···O, or $\dot{O}\cdot\dot{O}$ according to the Linnett notation[21,36-38]) between the oxygen atoms of a carboxylate ligand. The results of the present study show that the latter type of covalent–ionic resonance is primarily responsible for the antiferromagnetism of copper(II) carboxylate dimers. Each of them involves the transfer of one electron between the two oxygen atoms of a carboxylate ligand, and therefore the magnitudes of the Hamiltonian matrix elements H_{26} and H_{48} depend on the magnitude of the O–O overlap integral.

For all of the D_{2h}-symmetry calculations that have been discussed so far, the $^3B_{1u}$ state is the $S = 1$ state of lowest energy. The values of $-2J$ for the $^3B_{2u}$ state (Table II) may approach that for $^3B_{1u}$ and may sometimes lie below it.

de Loth et al.[18] have provided an ab initio MO perturbation analysis of the origin of the antiferromagnetism of copper acetate. Three types of contributions to the magnitude of the exchange parameter were considered, namely direct exchange, superexchange, and spin polarization. The direct exchange was associated with the spin-couplings of the two magnetic electrons when they occupied separate MOs of the general form $a \simeq d_A + t$ and $b \simeq d_B + t'$, in which d_A and d_B are the $d_{x^2-y^2}$ AOs, and t and t′ are acetate MOs. For one acetate ligand, this form of direct exchange corresponds approximately to resonance between the covalent structures **1**–**3** of the present VB treatment. de Loth et al. have calculated a value of -230 cm^{-1} for the direct exchange contribution to $-2J$. This ferromagnetic contribution arises because eq 3–5 of ref 18 ignore the overlap integral S_{ab} for the magnetic orbitals a and b. When this integral is included, as it is in the present VB treatment, the "direct exchange" contribution

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(39) Tokii, T.; Muto, Y. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 1549.
(40) Porter, L. C.; Doedens, R. J. *Inorg. Chem.* **1984**, *23*, 997.

to $-2J$ is antiferromagnetic, and its value ranges from 2–3 cm^{-1} (as in **1**) to 590–770 cm^{-1} (as in **3**) when one acetate ligand is considered.

Conclusions

The results of these nonempirical VB calculations support the conclusion obtained from earlier MO–CI and VB studies[15] that O–O overlap within the carboxylate ligands is primarily responsible for the antiferromagnetism that is observed for Cu(II) carboxylate dimers. The resulting stabilization of the $S = 0$ state relative to the $S = 1$ state arises primarily from covalent–ionic resonance of the Pauling "3-electron bond" type, i.e., it leads to the development of this type of bond $(\dot{O}\cdot\dot{O})$ between the oxygen atoms of the carboxylate ligands. The "cis O–O overlap" contributions to the rotation barriers for N_2O_4,[24e-h,41] N_2O_3,[41] and related molecules are also associated with the development of in-plane Pauling "3-electron bonds" between pairs of cis oxygen atoms in the planar conformers.

Acknowledgment. We thank the Australian Research Grants Scheme for financial support for this project. One of us (F.L.S.) acknowledges the award of a University of Melbourne Postgraduate Scholarship.

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(41) Harcourt, R. D.; Skrezenek, F. L.; Volkoff, C., in preparation.

Electrochemical Oxidation of the Tetrakis(μ-pyrophosphito-P,P')diplatinum(II) Complex $Pt_2(\mu-P_2O_5H_2)_4^{4-}$ Both in the Presence and the Absence of Halide Ions, and Reduction of the Axially Substituted Halodiplatinum(III) Complexes $Pt_2(\mu-P_2O_5H_2)_4X_2^{4-}$

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Abstract: In the presence of added halide ions X^- (X = Cl, Br, I), aqueous solutions of the complex $Pt_2(\mu-P_2O_5H_2)_4^{4-}$ can be electrochemically oxidized to $Pt_2(\mu-P_2O_5H_2)_4X_2$.$^{4-}$ Lowering the potential causes the reaction to reverse. The OTTLE cell data for all three reactions show isosbestic points and no intermediates. The potential required for the oxidation of $Pt_2(\mu-P_2O_5H_2)_4^{4-}$ and the reduction of $Pt_2(\mu-P_2O_5H_2)_4X_2^{4-}$ depends on X. By differential pulse polarography at a glassy carbon electrode the peak potential for oxidation is 0.69 V, and with added Cl^-, Br^-, and I^- the respective potentials are 0.56, 0.37, and −0.03 V vs. Ag/AgCl. The peak potentials for reduction of $Pt_2(\mu-P_2O_5H_2)_4X_2^{4-}$ for X = Cl, Br, and I are −0.11, −0.18, and −0.21 V, respectively. The complex $Pt_2(\mu-P_2O_5H_2)_4^{4-}$ reduces at a potential of −0.43 V in the presence of magnesium ion. The cyclic voltammograms in aqueous solution with added halide ion show irreversible behavior with $E_{pa} - E_{pc}$ values of 0.86, 0.65, and 0.29 V for X = Cl, Br, and I. Rapid scan (1000 V/s) cyclic voltammetry in acetonitrile solvent with no added halide ion shows irreversible behavior with oxidation and reduction waves at 1.12 and 0.61 V. The electrochemical data are explained on the basis of halide ion adsorption at the electrode surface.

The diplatinum(II) complex anion $Pt_2(\mu-P_2O_5H_2)_4^{4-}$ has attracted interest primarily because of its intense luminescence in aqueous solution at ambient temperature.[1] The ground- and excited-state chemistry of this complex can be rationalized on the basis of Gray's simplified molecular orbital model for binuclear complexes.[2] In this model the close separation between the planar d^8 metal centers causes the d_{z^2} and p_z orbitals to split into bonding and antibonding pairs. The ground-state electron configuration of $Pt_2(\mu-P_2O_5H_2)_4^{4-}$ is $d\sigma^2 d\sigma^{*2}$, and the excited-state configuration is $d\sigma^2 d\sigma^{*1} p\sigma^1$. Electron-transfer reactions with these two states has been the source of much interest, but there is no published work describing the electrochemistry of these complexes.

The Pt_2(II) complex $Pt_2(\mu-P_2O_5H_2)_4^{4-}$ will undergo two-electron oxidation to give products having Pt_2(III) centers. If this oxidation is effected with halogens X_2 (X = Cl, Br, I) the product is $Pt_2(\mu-P_2O_5H_2)_4X_2$.$^{4-}$ Alternatively the oxidation can be effected with one-electron oxidants such as ceric ion or hexachloroiridate(IV). In the presence of halide ion the product is again $Pt_2(\mu-P_2O_5H_2)_4X_2^{4-}$, but with Ce^{4+} in the absence of added halide ion the complex $Pt_2(\mu-P_2O_5H_2)_4(H_2O)_2^{2-}$ is formed. In reverse, the conversion of $Pt_2(\mu-P_2O_5H_2)_4X_2^{4-}$ to $Pt_2(\mu-P_2O_5H_2)_4^{4-}$ can be accomplished by using acidified zinc, ascorbic acid, sulfite ion, or hydrogen as reductants. No intermediates have been observed in these transformations.[3] By contrast the reduction of $Pt_2(\mu-P_2O_5H_2)_4^{4-}$ to either the Pt_2(I,II) or the Pt_2(I) complexes $Pt_2(\mu-P_2O_5H_2)_4^{5-}$ and $Pt_2(\mu-P_2O_5H_2)_4^{6-}$ has been reported.[4] The former complex has been observed by pulse radiolysis techniques, and the latter anion is reported formed by the chromous ion reduction of the Pt_2(II,II) ground state.

Electron-transfer reactions with the excited state $Pt_2(\mu-P_2O_5H_2)_4^{4-*}$ have also been reported. Quenching studies show that this state is both a strong oxidant and reductant, and in the photoinduced addition of aryl halides to $Pt_2(\mu-P_2O_5H_2)_4^{4-}$ it has been proposed that the pathway involves an $S_{RN}1$ electron-transfer mechanism from the excited state to the aryl halide.[5] Although

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(1) Sperline, R. P.; Dickson, M. K.; Roundhill, D. M. *J. Chem. Soc., Chem. Commun.* **1977**, 62–63.

(2) Mann, K. R.; Gordon, J. G., II.; Gray, H. B. *J. Am. Chem. Soc.* **1981**, *103*, 7061–7064.

(3) Bryan, S. A.; Dickson, M. K.; Roundhill, D. M. *J. Am. Chem. Soc.* **1984**, *106*, 1882–1883. Che, C.-M.; Butler, L. G.; Grunthaner, P. J.; Gray, H. B. *Inorg. Chem.* **1985**, *24*, 4662–4665.

(4) Che, C.-M.; Atherton, S. J.; Butler, L. G.; Gray, H. G. *J. Am. Chem. Soc.* **1984**, *106*, 5143–5145. Alexander, K. A.; Stein, P.; Hedden, D. B.; Roundhill, D. M. *Polyhedron* **1983**, *2*, 1389–1392.

(5) Roundhill, D. M. *J. Am. Chem. Soc.* **1985**, *107*, 4354–4356.

0002-7863/86/1508-5408$01.50/0