

$\text{Ni}^{\text{II}}(\text{H}_3\text{G}_4\text{A})^{2-}$ , 62882-73-9;  $\text{Cu}^{\text{II}}(\text{H}_3\text{G}_3\text{AOCH}_3)^-$ , 62882-66-0;  $\text{Cu}^{\text{II}}(\text{H}_3\text{G}_4\text{AOCH}_3)^-$ , 62882-65-9;  $\text{Ni}^{\text{II}}(\text{H}_3\text{G}_3\text{AOCH}_3)^-$ , 62006-85-3;  $\text{Ni}^{\text{II}}(\text{H}_3\text{G}_4\text{AOCH}_3)^-$ , 62882-64-8;  $\text{Cu}^{\text{III}}(\text{H}_3\text{A}_5)^-$ , 62882-63-7;  $\text{Cu}^{\text{III}}(\text{H}_3\text{V}_4)^-$ , 62959-93-7;  $\text{Ni}^{\text{III}}(\text{H}_3\text{A}_4)^-$ , 62882-62-6;  $\text{Ni}^{\text{III}}(\text{H}_3\text{A}_5)^-$ , 62882-61-5.

## References and Notes

- (1) E. W. Wilson, Jr., and R. B. Martin, *Inorg. Chem.*, **10**, 1197 (1971).
- (2) J. M. Tsangaris and R. B. Martin, *J. Am. Chem. Soc.*, **92**, 4255 (1970).
- (3) J. W. Chang and R. B. Martin, *J. Phys. Chem.*, **73**, 4277 (1969).
- (4) G. F. Bryce and F. R. N. Gurd, *J. Biol. Chem.*, **241**, 1439 (1966).
- (5) A. E. Martell, M. K. Kim, and A. Kaneda, *J. Coord. Chem.*, **4**, 159 (1975).
- (6) T. Yasui, J. Hidaka, and Y. Shimura, *Bull. Chem. Soc. Jpn.*, **39**, 2417 (1966).
- (7) C. J. Hawkins and P. J. Lawson, *Inorg. Chem.*, **9**, 6 (1970).
- (8) G. C. Dellenback and B. E. Douglas, *Inorg. Nucl. Chem. Lett.*, **9**, 1255 (1973).
- (9) C. J. Hawkins and G. A. Lawrance, *Inorg. Nucl. Chem. Lett.*, **9**, 483 (1973).
- (10) C. Djerassi and L. E. Geller, *J. Am. Chem. Soc.*, **81**, 2789 (1959).
- (11) K. A. Jensen, S. Burmester, G. Cederberg, R. B. Jensen, C. Pedersen, and E. Larsen, *Acta Chem. Scand.*, **19**, 1239 (1965).
- (12) M. K. Kim and A. E. Martell, *J. Am. Chem. Soc.*, **89**, 5138 (1967).
- (13) G. H. Nancollas and D. J. Poulton, *Inorg. Chem.*, **8**, 680 (1969).
- (14) A. Keneda and A. E. Martell, *J. Coord. Chem.*, **4**, 140 (1975).
- (15) C. R. Hartzell and F. R. N. Gurd, *J. Biol. Chem.*, **244**, 147 (1969).
- (16) H. C. Freeman, J. M. Guss, and R. L. Sinclair, *Chem. Commun.*, 485 (1968).
- (17) H. C. Freeman and M. R. Taylor, *Acta Crystallogr.*, **18**, 939 (1965).
- (18) H. C. Freeman, *Adv. Protein Chem.*, **22**, 257 (1967).
- (19) J. F. Blount, R. V. Holland, and H. C. Freeman, unpublished observations (1966) quoted in ref 27, p 406.
- (20) R. J. Angelici and D. Hopgood, *J. Am. Chem. Soc.*, **90**, 2514 (1968).
- (21) R. Nakon and R. J. Angelici, *J. Am. Chem. Soc.*, **95**, 3170 (1973).
- (22) D. A. Buckingham and M. Wein, *Inorg. Chem.*, **13**, 3207 (1974).
- (23) D. A. Buckingham, D. M. Foster, and A. M. Sargeson, *J. Am. Chem. Soc.*, **90**, 6032 (1968).
- (24) D. A. Buckingham, D. M. Foster, L. G. Marzilli, and A. M. Sargeson, *Inorg. Chem.*, **9**, 11 (1970).
- (25) D. W. Margerum, K. L. Chellappa, F. P. Bossu, and G. L. Burce, *J. Am. Chem. Soc.*, **97**, 6894 (1975).
- (26) F. P. Bossu and D. W. Margerum, *J. Am. Chem. Soc.*, **98**, 4003 (1976).
- (27) F. P. Bossu, K. L. Chellappa, and D. W. Margerum, *J. Am. Chem. Soc.*, **99**, 2195 (1977).
- (28) D. W. Margerum, L. F. Wong, F. P. Bossu, K. L. Chellappa, J. J. Czarnecki, S. T. Kirsey, Jr., and T. A. Neubecker, *Adv. Chem. Ser.*, in press.
- (29) B. R. Clark and D. H. Evans, *J. Electroanal. Chem.*, **69**, 181 (1976).
- (30) A. Abu-Shumays and J. Duffield, *Anal. Chem.*, **38**, 29A (1966).
- (31) S. Kirschner, *Coord. Chem. Rev.*, **2**, 461 (1967).
- (32) C. J. Hawkins, "Absolute Configuration of Metal Complexes", Wiley-Interscience, New York, N.Y., 1971, p 157.
- (33) G. L. Burce and D. W. Margerum, submitted for publication.
- (34) G. L. Burce, Ph.D. Thesis, Purdue University, W. Lafayette, Ind., 1975.
- (35) U. Meresaar and A. Agren, *Acta Pharm. Suec.*, **5**, 85 (1968).
- (36) W. J. Kauzmann, J. E. Walter, and H. Eyring, *Chem. Rev.*, **26**, 339 (1940).
- (37) S. F. Mason, *Q. Rev., Chem. Soc.*, **17**, 20 (1963).
- (38) W. Moffit and A. Moscowitz, *J. Chem. Phys.*, **30**, 648 (1959).
- (39) A. E. Martell and M. K. Kim, *J. Coord. Chem.*, **4**, 9 (1974).
- (40) W. J. Kauzmann, J. E. Walter, and H. Eyring, *Chem. Rev.*, **26**, 339 (1940).
- (41) O. Yamauchi, Y. Nakao, and A. Nakahara, *Bull. Chem. Soc. Jpn.*, **48**, 2572 (1975).

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## Paramagnetic M(I) Complexes Generated by the Electrochemical Reduction of M(II) Nickel, Palladium, and Platinum 1,2-Dithiolates

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Received February 25, 1977

AIC70153K

The electrochemical reduction of square-planar nickel, palladium, and platinum complexes of the maleonitriledithiolate (mnt) ligand have been investigated. In each case, reduction of the  $\text{M}^{\text{II}}(\text{mnt})_2^{2-}$  species in nonaqueous solvents proceeded by a one-electron process, shown to be reversible by cyclic voltammetry and ac polarography. ESR spectra obtained for  $\text{Pd}(\text{mnt})_2^{3-}$  and nickel-61 enriched  $\text{Ni}(\text{mnt})_2^{3-}$  were consistent with the formulation of these species as  $d^9$  metals with the unpaired electron in an orbital consisting of contributions from the  $d_{xy}$  metal orbital and in-plane sulfur orbitals. More covalency is found in the palladium complex than in the nickel complex. The reduction of  $\text{Pt}(\text{mnt})_2^{2-}$  proceeds by two successive one-electron processes. Arguments based on these data are presented which suggest a ground state for  $\text{Pt}(\text{mnt})_2^{3-}$  which may be different from its Ni or Pd analogue.

### Introduction

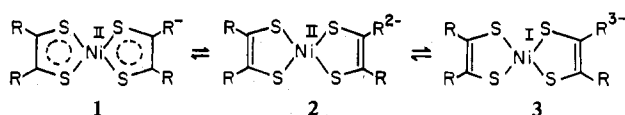
Although metal(I) complexes of nickel, palladium, and platinum have been proposed as intermediates in a number of reactions,<sup>1-5</sup> direct experimental evidence and isolation of such complexes have been rare. In fact, most known Ni(I) complexes and all isolated Pd(I) and Pt(I) complexes are binuclear in nature, giving diamagnetic metal-metal bonded or ligand-bridged bimetallic species.<sup>6</sup> In previous communications<sup>7-9</sup> we have established the existence of mononuclear  $d^9$  complexes of Ni, Pd, and Pt produced by the reversible one-electron reduction of  $d^8$  metal dithiolate complexes. In this paper we offer a fuller exposition of both the voltammetric data and electron spin resonance (ESR) results on these reduced complexes.

Naturally, ESR spectroscopy, so successfully employed in the study of  $d^9$  copper complexes, is a powerful tool for study of the electronic structures of the nickel group  $d^9$  complexes. Therefore, it is somewhat surprising that even in the case of nickel, for which a respectable number of  $d^9$  complexes are now known,<sup>10</sup> very little ESR work has been reported. Besides our earlier report on  $\text{Ni}(\text{mnt})_2^{3-}$ <sup>7</sup> and the work of Busch and co-workers on reduced nickel macrocycles,<sup>11</sup> only signals from trapped Ni(I), arising from x irradiation of  $\text{Ni}(\text{CN})_4^{2-}$ <sup>12</sup> and

nickel-doped glasses,<sup>13</sup> have been reported. Two other studies, in which signals from nickel(I) impurities in ternary chalcopyrites and ZnSe were observed,<sup>14,15</sup> are apparently the only ones reporting  $^{61}\text{Ni}$  hyperfine splittings ( $^{61}\text{Ni}$ ,  $I = 3/2$ , 1.2% abundance). In this paper we report the  $^{61}\text{Ni}$ -enriched ESR spectrum of  $\text{Ni}(\text{mnt})_2^{3-}$ .

In contrast to nickel, stable paramagnetic  $d^9$  complexes of Pd and Pt are apparently unknown. Several papers have appeared in which Pd(II) complexes were irradiated and studied by ESR at 77 °K,<sup>16-20</sup> but the signals ascribed to Pd(I) disappeared upon warming of the matrix. A similar study involving irradiation of  $\text{K}_2\text{PtCl}_4$  resulted in several platinum-containing radicals, including a signal attributed to  $[\text{PtCl}_4]^{3-}$ ,<sup>21</sup> and  $[\text{PtBr}_6]^{5-}$  has been postulated as the photolysis product of Pt(II) in AgBr matrices.<sup>22</sup>

In this work we have studied the electrochemical reduction of dianions of the square-planar metal(II) 1,2-dithiolate complexes  $\text{M}(\text{mnt})_2^{2-}$  (**2**, R = CN). In addition to providing



some unique M(I) complexes, this work also provided a rare opportunity to compare ESR results on different members of an electron-transfer series, in this case by comparing the ESR of the reduced dithiolates (3) with those<sup>23-26</sup> of the oxidized forms (1).

### Experimental Section

**Chemicals.**  $\text{Na}_2\text{mnt}$ ,  $(\text{Bu}_4\text{N})_2[\text{Ni}(\text{mnt})_2]$ ,  $(\text{Bu}_4\text{N})_2[\text{Pd}(\text{mnt})_2]$ , and  $(\text{Bu}_4\text{N})_2[\text{Pt}(\text{mnt})_2]$  were prepared by the literature methods<sup>27</sup> and recrystallized several times.  $^{61}\text{Ni}$ -enriched  $\text{Ni}(\text{mnt})_2^{2-}$  was produced from nickel metal by the following procedure. Nickel (8.1 mg) enriched to about 90% in  $^{61}\text{Ni}$  (Oak Ridge National Laboratories) was slowly digested with concentrated  $\text{HNO}_3$  until virtual dryness. Distilled water (10 mL) was added to the flask followed by 55 mg of  $\text{Na}_2\text{mnt}$  dissolved in 4 mL of a 1:1  $\text{EtOH-H}_2\text{O}$  mixture. To the resulting red solution was added 120 mg of  $\text{Bu}_4\text{NI}$  dissolved in 5 mL of  $\text{EtOH}$ . After cooling overnight the red precipitate was collected and washed with water. After vacuum drying a yield of about 90 mg (theory 110 mg) was obtained.

Acetonitrile (Eastman Spectrograde) was stored under vacuum over calcium hydride and then vacuum distilled immediately before use. 1,2-Dimethoxyethane (glyme) was treated similarly with lithium aluminum hydride.  $\text{Bu}_4\text{NPF}_6$  was prepared by mixing hot acetone solutions of  $\text{Bu}_4\text{NI}$  (Southwestern Analytical Chemicals) and  $\text{NH}_4\text{PF}_6$  followed by (hot) filtration and subsequent precipitation of the product by addition of water. The resulting electrolyte was recrystallized several times from ethanol and vacuum dried for 24 h at 100 °C. Mercury was triply distilled and nitrogen was of a prepurified grade.

**Electrochemistry.** Most of the electrochemical work was performed at ambient pressure on solutions which were deoxygenated by purging with nitrogen. In these experiments the vacuum distilled solvent was transferred in a drybag to a volumetric flask containing sufficient  $\text{Bu}_4\text{NPF}_6$  and electroactive compound to make the solution about 0.1 and  $5 \times 10^{-4}$  M in these compounds, respectively. The resulting solution was transferred in the drybag to a voltammetry cell (Metrohm style) and the cell was removed from the drybag and purged with solvent-saturated nitrogen during the course of the experiment. The bulk reduction of  $\text{Pd}(\text{mnt})_2^{2-}$  in  $\text{CH}_3\text{CN}$  was also studied in the vacuum cell described earlier,<sup>8</sup> to ensure rigorous exclusion of oxygen.

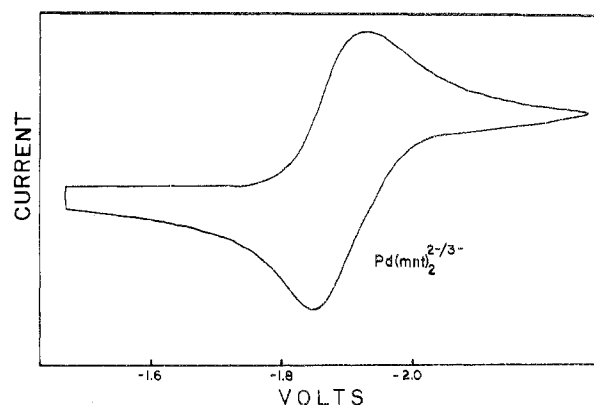
Several electrochemical instruments were employed. Polarography, cyclic voltammetry, and bulk electrolyses were accomplished with the Princeton Applied Research (PAR) Model 173 and associated peripheral equipment, as described previously.<sup>8</sup> Differential pulse polarography was performed using the PAR Model 174A polarographic analyzer and the ac polarographic data were taken on the PAR Model 170 electrochemistry system. All potentials are referred to the aqueous saturated calomel electrode (SCE).

**Electron Spin Resonance Measurements.** ESR data were taken on a Varian V-4502 spectrometer system using DPPH as a *g*-value standard in a dual cavity arrangement. Samples for ESR were prepared by electrolysis of the diamagnetic M(II) dianions of the dithiolates in one of several ways. Anisotropic spectra of  $\text{Ni}(\text{mnt})_2^{3-}$  were obtained after electrolysis of an approximately 1 mM solution of  $\text{Ni}(\text{mnt})_2^{2-}$  in  $\text{CH}_3\text{CN}/0.1$  M  $\text{Bu}_4\text{NPF}_6$  at a platinum wire at -2 V in an intra muros cell of conventional design,<sup>28</sup> followed by freezing of the solution at about -100 °C. Solution spectra of  $\text{Ni}(\text{mnt})_2^{3-}$  were obtained by electrolysis at -2 V at a platinum flag in a flat electrolysis cell.  $\text{Pd}(\text{mnt})_2^{3-}$  was produced by electrolysis of  $\text{Pd}(\text{mnt})_2^{2-}$  at -2.1 V at a mercury pool in  $\text{CH}_3\text{CN}$ . The orange solution of the trianion was transferred in a drybag to either a flat cell (for solution spectra) or a quartz 3 mm tube which was frozen at -100 °C (for glassy spectra). Computer simulations of ESR spectra were obtained using a modification of the program of Hove et al.<sup>29</sup> on a Xerox Sigma-6 computer.

### Electrochemical Data

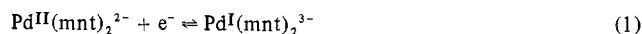
**Ni(mnt)<sub>2</sub><sup>2-</sup> Reduction.** The highly reversible  $\text{Ni}(\text{II}) \rightleftharpoons \text{Ni}(\text{I})$  reduction of the  $\text{Ni}(\text{mnt})_2$  dianion ( $E_{1/2} = -1.67$  V in  $\text{CH}_3\text{CN}$ ) has been fully characterized in previous work<sup>7,8</sup> and will not be further discussed, except in terms of the electronic structure of the trianion.

**Pd(mnt)<sub>2</sub><sup>2-</sup> Reduction.** The  $\text{Pd}(\text{mnt})_2^{2-}$  ion can be reduced in a single one-electron reversible reduction to the formally Pd(I) species,  $\text{Pd}(\text{mnt})_2^{3-}$ . This  $\text{Pd}(\text{II}) \rightleftharpoons \text{Pd}(\text{I})$  couple was studied in a variety of nonaqueous media, including aceto-



**Figure 1.** Cyclic voltammogram at  $v = 100$  mV/s of  $5 \times 10^{-4}$  M  $\text{Pd}(\text{mnt})_2^{2-}$  in  $\text{CH}_3\text{CN}/\text{Bu}_4\text{NPF}_6$  at a hanging mercury drop electrode.

nitrile, acetone, and glyme. A typical cyclic voltammogram is shown in Figure 1.  $E_{1/2}$  varied from -1.90 to -1.93 V in these solvents (-1.90 V in  $\text{CH}_3\text{CN}$ ), and since the character of the reduction did not appear to change as a function of solvent, only representative data are presented. For example, in glyme CV data were collected over the range of scan rates 24 mV/s to 8 V/s. The ratio of the anodic-to-cathodic peak current was  $1.00 \pm 0.01$  and the current function (cathodic peak current divided by square root of scan rate) changed by less than 2% over this interval. At scan rates up to about 500 mV/s, the peak current separations,  $e_{pa} - e_{pc}$ , were 60-65 mV, and at faster scan rates increased peak separations were ascribed primarily to solution resistance effects. All these data are consistent with the mechanism for the  $\text{Pd}(\text{mnt})_2^{2-}$  reduction being the simple process 1 uncomplicated by coupled chemical reactions.



The Pd(I) complex was stable when generated in acetonitrile under strictly anaerobic conditions. Bulk coulometry in the vacuum line cell described earlier<sup>8</sup> gave  $n(\text{apparent}) = 1.0$  as the electrolysis proceeded at -2.1 V from the green Pd(II) solution to the orange Pd(I) solution. In a separate experiment using a conventional cell it was possible to generate the Pd(I) species under nitrogen, in a drybag, and to syringe it into ESR sample tubes. Solutions of the Pd(I) complex were quantitatively reoxidized back to the starting Pd(II) complex by electrolysis at -1.5 V.

**Pt(mnt)<sub>2</sub><sup>2-</sup> Reduction.**  $\text{Pt}(\text{mnt})_2^{2-}$  behaves quite differently than the other complexes in this series, in that it shows two closely spaced reduction waves. The half-wave potentials in  $\text{CH}_3\text{CN}$ , measured as the potential at which the cathodic currents in cyclic voltammetry are 85% of their peak values, are about -2.22 and -2.44 V (these values supercede those reported earlier<sup>9</sup>). Figure 2 shows a cyclic voltammogram of these two waves, as well as the first alone, in acetonitrile. The second wave persisted up to very rapid scan rates, eliminating the possibility that it results from the product of a follow-up reaction from the preceding wave. The reversibility of the first wave was established by two experiments: (a) cyclic voltammetry in which the scan was "clipped" as closely as possible to the first peak showed an anodic peak in the positive-going scan direction, and (b) ac polarography showed a well-defined peak at the potential of the first wave. Figure 2 demonstrates the in-phase component of the ac current at 100 Hz, and the relative heights of the two waves is consistent with a more rapid electron transfer rate ( $k_s$ ) in the first reduction.

The lack of good separation between the two waves has restricted us to conclusions based on qualitative data, but dc and ac polarography and cyclic voltammetry are consistent with the following: (a) each reduction is a one-electron process,

Table I. ESR Parameters for Metal-mnt Complexes<sup>a</sup>

Confign	Complex	$g_1$	$g_2$	$g_3$	$A_1^b$	$A_2^b$	$A_3^b$	$A_{iso}^b$	$P/P_0$	$K$
"d <sup>7</sup> " <sup>c</sup>	Ni(mnt) <sub>2</sub> <sup>2-</sup>	2.160	2.042	1.998	(-)15	(+)2.9	<2	(-)4.6	0.24	0.21
d <sup>9</sup>	Ni(mnt) <sub>2</sub> <sup>3-</sup>	2.205	2.081	2.061	(-)53	(+)5.8	(+)5.8	(-)5.8	0.85	0.27
					(-)53	(-)5.8	(-)5.8	(-)5.8	0.70	0.42
"d <sup>7</sup> " <sup>c</sup>	Pd(mnt) <sub>2</sub> <sup>2-</sup>	2.070	2.044	1.956	(+)9.0	(+)6.3	(+)5.5	(+)8.2	0.19	1.30
d <sup>9</sup>	Pd(mnt) <sub>2</sub> <sup>3-</sup>	2.116	2.042	2.034	(+)44	(+)29	(+)26	(+)30	0.45	1.22
d <sup>9</sup>	Cu(mnt) <sub>2</sub> <sup>2-</sup>	2.086	2.026	2.023	(-)162	(-)39	(-)39	(-)80	0.45	0.55

<sup>a</sup> Data for Ni(mnt)<sub>2</sub><sup>2-</sup>, Pd(mnt)<sub>2</sub><sup>2-</sup>, and Cu(mnt)<sub>2</sub><sup>2-</sup> taken from Maki and co-workers.<sup>23,25</sup> <sup>b</sup> Hyperfine splittings in cm<sup>-1</sup> × 10<sup>4</sup>; signs are based on assumptions made in the text and in references. <sup>c</sup> The formalism of the electron configuration of the oxidation state is, of course, inadequate for the complexes Ni(mnt)<sub>2</sub><sup>2-</sup> and Pd(mnt)<sub>2</sub><sup>2-</sup>, and these systems are more rigorously referred to as spin-delocalized complexes.

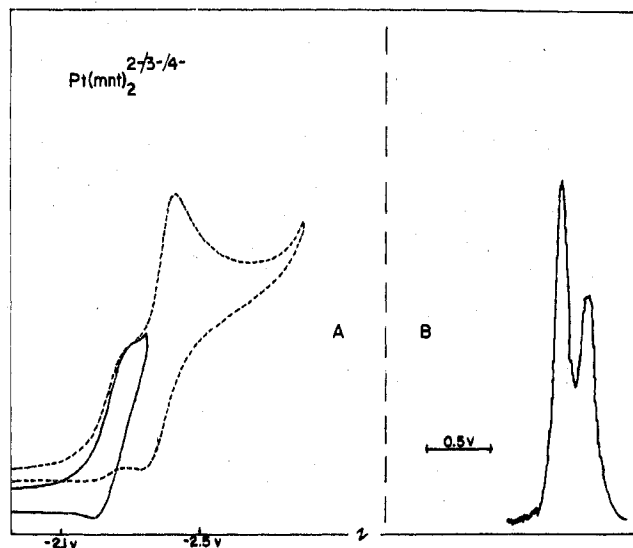


Figure 2. Voltammetry of  $5 \times 10^{-4}$  M Pt(mnt)<sub>2</sub><sup>2-</sup> in CH<sub>3</sub>CN/Bu<sub>4</sub>NPF<sub>6</sub>: (A) cyclic voltammogram at  $v = 180$  mV/s of first reduction alone (solid line) and both reductions together (dotted line); (B) sampled ac polarogram at 100 Hz of in-phase component of ac current.

(b) the first reduction (eq 2) [to Pt(mnt)<sub>2</sub><sup>3-</sup>] is chemically

$$\text{Pt(mnt)}_2^{2-} + e^- \rightleftharpoons \text{Pt(mnt)}_2^{3-} \quad (2)$$

(3) the second reduction (eq 3) [to Pt(mnt)<sub>2</sub><sup>4-</sup>] is chemically

$$\text{Pt(mnt)}_2^{3-} + e^- \rightleftharpoons \text{Pt(mnt)}_2^{4-} \quad (3)$$

reversible at slow CV scan rates, (c) the first reduction is chemically irreversible when the first and second waves are scanned together (Figure 2), (d) the second reduction (eq 3) [to Pt(mnt)<sub>2</sub><sup>4-</sup>] is chemically reversible at least at fast scan rates, and (e) the heterogeneous electron transfer rate is lower for the second reduction than for the first.

The observation that the first reduction becomes irreversible when the two waves are scanned together suggests that the Pt(mnt)<sub>2</sub><sup>4-</sup> formed in the second reduction reacts with Pt(mnt)<sub>2</sub><sup>3-</sup> to expend the latter at the electrode surface. It does not appear to us that a disproportionation mechanism can account for the experimental facts, and we do not suggest an alternate mechanism at this time. The factor pertinent to this study, however, is the observation of two, rather than one, reversible reductions of the Pt(II) complex. Without ESR data to establish the nature of the half-occupied orbital in Pt(mnt)<sub>2</sub><sup>3-</sup>, one cannot identify the trianion as a Pt(I) species, and due to the obvious limited stability of that ion, ESR experiments were not attempted. The question of the orbital ordering in the Pt(mnt)<sub>2</sub><sup>2-</sup> complex is deferred to the discussion below.

**M[S<sub>2</sub>C<sub>2</sub>(CF<sub>3</sub>)<sub>2</sub>]<sub>2</sub><sup>2-</sup> Complexes.** Ni[S<sub>2</sub>C<sub>2</sub>(CF<sub>3</sub>)<sub>2</sub>]<sub>2</sub><sup>2-</sup> can be reversibly reduced to the corresponding Ni(I) trianion,<sup>8</sup> so we sought to investigate the reduction of the corresponding Pd and Pt anions. Therefore, the voltammetry of (*N*-methylphenazinium)<sup>+</sup>(Pt[S<sub>2</sub>C<sub>2</sub>(CF<sub>3</sub>)<sub>2</sub>]<sub>2</sub><sup>2-</sup>) and (*N*-methylpyridinium)<sup>+</sup>(Pd[S<sub>2</sub>C<sub>2</sub>(CF<sub>3</sub>)<sub>2</sub>]<sub>2</sub><sup>2-</sup>) was pursued. In neither case was

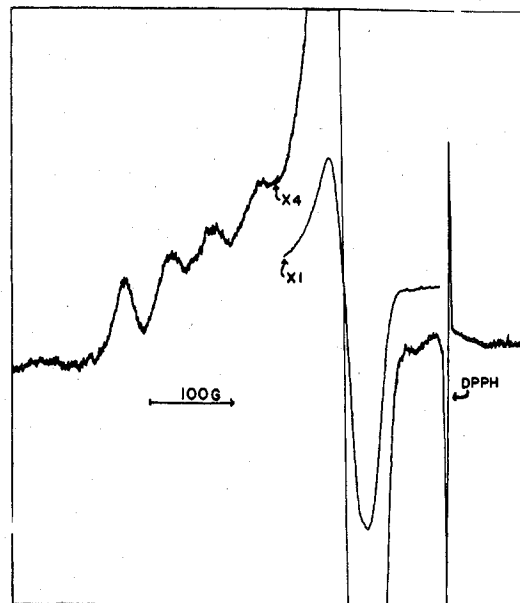


Figure 3. ESR spectrum of frozen solution ( $-100$  °C) of <sup>61</sup>Ni enriched Ni(mnt)<sub>2</sub><sup>3-</sup> in acetonitrile. X1 denotes a trace taken at lower sensitivity than X4 to put higher field portion on scale.

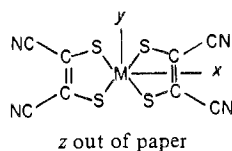
a reduction observed which might be ascribed to the reduction of the M[S<sub>2</sub>C<sub>2</sub>(CF<sub>3</sub>)<sub>2</sub>]<sub>2</sub> dianion. In each case, the only reduction other than the MS<sub>4</sub><sup>2-</sup> ⇌ MS<sub>4</sub><sup>3-</sup> couple was that due apparently to the cationic counterion.<sup>30</sup>

### ESR Results

**Ni<sup>I</sup>(mnt)<sub>2</sub><sup>3-</sup>.** An observed earlier,<sup>7</sup> the spectrum of a frozen solution of natural (i.e., unenriched) Ni(mnt)<sub>2</sub><sup>3-</sup> shows a rhombic  $g$  tensor, although the deviation from axial symmetry is small in the high-field components ( $g_2 - g_3 = 0.02$ ). The 90% <sup>61</sup>Ni enriched sample has the appearance of an axially symmetric spectrum (Figure 3) because the small high-field nickel splittings produce a single, inhomogeneously broadened, high-field line. The low-field (now  $g_{||}$ ) region shows a well-resolved quartet due to interaction with a single <sup>61</sup>Ni nucleus ( $I = 3/2$ ). The magnitude of  $A_{\perp}$ (Ni) was obtained by matching of computer simulated spectra with the experimental spectrum, using  $g$  values and line widths derived from spectra of natural Ni(mnt)<sub>2</sub><sup>3-</sup> under nominally identical conditions. We judge the maximum error in this method to be about 2 gauss. Splittings are as given in Table I. The large nickel  $A_{||}$  splitting was assigned as negative, as predicted by eq 7 and the value of  $P_0$  for nickel, which is predicted to be positive (vide infra).

By analogy with the results of Maki et al.<sup>23</sup> on the iso-electronic Cu<sup>II</sup>(mnt)<sub>2</sub><sup>2-</sup>, it was previously predicted that Ni(mnt)<sub>2</sub><sup>3-</sup> has a 3b<sub>1g</sub> ground state,<sup>7</sup> composed of a metal d<sub>xy</sub> contribution and in-plane sulfur p orbitals (coordinate system given below).

Now that the nickel hyperfine splittings have been measured, it is possible to test this hypothesis. We use the equations 4–9



from Maki's treatment<sup>23</sup> for the  $d_{xy}$  ground state which relate the  $g$  and  $A$  values to the bonding parameters  $P$  and  $K$  by way of the configurational excitation energies,  $C_i$ .

$$g_{xx} = 2 - 2C_3 \quad (4)$$

$$g_{yy} = 2 - 2C_2 \quad (5)$$

$$g_{zz} = 2 - 8C_1 \quad (6)$$

$$A_{xx} = P[-2C_3 - K + 2/\gamma + 3/7C_2] \quad (7)$$

$$A_{yy} = P[-2C_2 - K + 2/\gamma + 3/7C_3] \quad (8)$$

$$A_{zz} = P[-8C_1 - K - 4/\gamma - 3/7(C_2 + C_3)] \quad (9)$$

$P$  and  $K$  are related to the anisotropic and isotropic parts, respectively, of the hyperfine tensor and are defined by eq 10 and 11. In this form,  $K$ , the Fermi contact term, is given in

$$P = g_e g_N \beta_e \beta_N \langle r^{-3} \rangle \quad (10)$$

$$K = (-2/3)\chi \frac{g_e g_N \beta_e \beta_N}{hca_0^3} / P \quad (11)$$

fractional units of  $P$ . In eq 10 and 11,  $g_N$  and  $\beta_N$  are the nuclear  $g$  value and nuclear magneton, respectively,  $\langle r^{-3} \rangle$  is the inverse cube electron-nuclear distance.  $\chi$  is as defined by Abragam, Horowitz, and Pryce<sup>31</sup> and is related to spin polarization of inner  $s$  orbitals by unpaired  $d$  electrons.<sup>32</sup>  $C_1 = \xi / (E_{x^2-y^2} - E_{xy})$ , where  $\xi$  is the effective spin-orbit coupling constant for Ni(I) and  $E_{x^2-y^2} - E_{xy}$  represents the energy difference between the orbital containing the unpaired electron ( $d_{xy}$ ) and the energy of  $d_{x^2-y^2}$  orbital. Similarly,  $C_2$  and  $C_3$  relate to excitations involving the  $d_{yz}$  and  $d_{zx}$  orbitals, respectively. The object of such a treatment is to see if the bonding parameters calculated assuming a certain ground state are reasonable and, if so, to obtain a measure of the metal-ligand covalency by noting the reduction of the measured  $P$  value from that calculated for the free metal ion,  $P_0$ , which has been given as  $102 \times 10^{-4} \text{ cm}^{-1}$  for Ni(I).<sup>14</sup> The ratio  $P/P_0$  is then the calculated value of the metal spin density.

Since eq 4-9 are overdetermined, we chose to treat the system as having an axially symmetric  $g$  tensor, with  $g_{\perp}$  being the average of  $g_2$  and  $g_3$ , 2.071. Frozen solution spectra arise from randomly oriented radicals and so cannot be used to assign directions to each of the anisotropic features of the spectrum. Consequently, we have assigned the  $z$  direction to the low-field large nickel splitting, in analogy to the single-crystal results on the isoelectronic Cu(II) system.<sup>23</sup> This assumption yielded quite reasonable values for  $P$  ( $87 \times 10^{-4} \text{ cm}^{-1}$  if  $A$  is positive,  $70 \times 10^{-4} \text{ cm}^{-1}$  if  $A$  is negative) and  $K$  (0.27 or 0.42, respectively) (Table II), whereas assignment of the low-field splitting to either the  $x$  or  $y$  direction did not. The ratio  $P/P_0$  of 0.7-0.8 establishes that the unpaired electron is quite highly localized in the metal ( $d_{xy}$ ) orbital and that rather little in-plane covalency exists in the Ni(I) complex.

Table II. Covalency Parameters for  $d^9$  Coordination Complexes

Metal	Complex	Method of productn	Covalency parameter	Meth- od of calculn	Ref
Ni	Ni(mnt) <sub>2</sub> <sup>3-</sup>	Electrolysis	0.70-0.85	$P/P_0$	This work
Pd	Pd(mnt) <sub>2</sub> <sup>3-</sup>	Electrolysis	0.45	$P/P_0$	This work
Pd	PdCl <sub>2</sub> <sup>3-</sup>	Irradiation	0.78	$\alpha^2$	16
Pd	Pd(acac) <sub>2</sub> <sup>-</sup>	Irradiation	0.74	$\alpha^2$	20
Cu	Cu(mnt) <sub>2</sub> <sup>2-</sup>	Stable	0.45	$P/P_0$	23
Cu	Cu(acac) <sub>2</sub>	Stable	0.81	$\alpha^2$	37

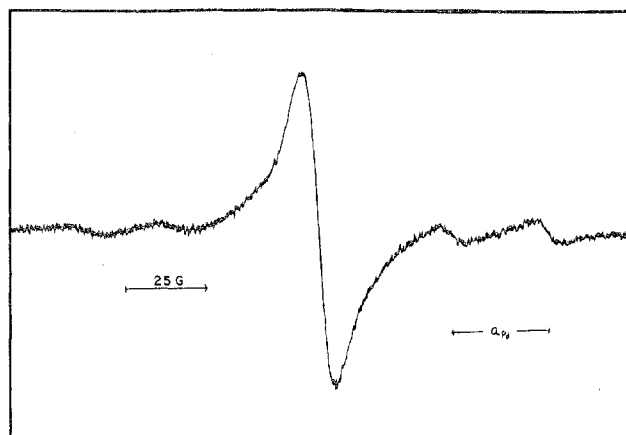


Figure 4. ESR spectrum of fluid solution of  $\text{Pd}(\text{mnt})_2^{3-}$  produced by electrolysis of an approximately  $10^{-3} \text{ M}$  solution of  $\text{Pd}(\text{mnt})_2^{2-}$  in  $\text{CH}_3\text{CN}/\text{Bu}_4\text{NPF}_6$  at  $-2.1 \text{ V}$ .

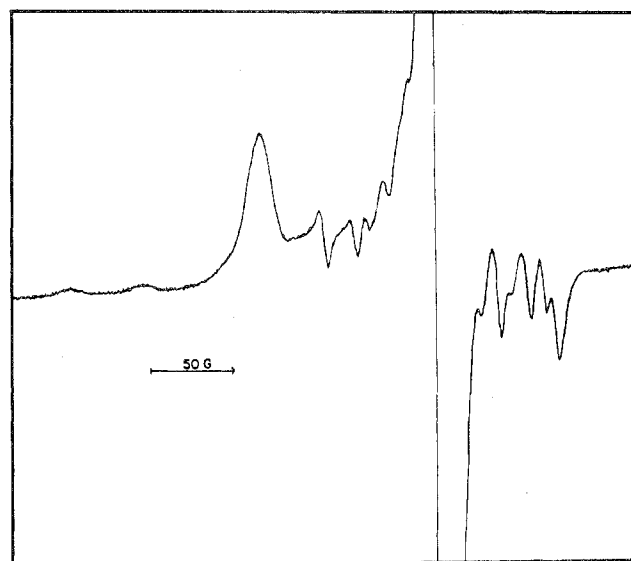


Figure 5. ESR of frozen solution ( $-196 \text{ }^\circ\text{C}$ ) of  $\text{Pd}(\text{mnt})_2^{3-}$  produced as in conditions of Figure 4.

In fact,  $\text{Cu}(\text{mnt})_2^{2-}$  shows considerably higher covalency ( $P/P_0 = 0.45$ ).<sup>23</sup>

**$\text{Pd}(\text{mnt})_2^{3-}$ .** The fluid solution and frozen solution spectra of this ion in acetonitrile are shown in Figures 4 and 5, respectively. The former clearly shows the presence of four of the six satellite lines expected for interaction of the unpaired electron with a single palladium-105 nucleus ( $I = 5/2$ , 22% abundant), with the two central components of the sextet hidden by the intense  $I = 0$  line. Interpretation of the frozen solution spectrum of the Pd(I) ion was straightforward except in the high-field region, where computer simulations could not duplicate the observed line intensities. Good agreement was obtained for the region to lower field of  $g_2$ , and the value of the high-field splitting can be estimated as 25 G from the position of  $g_3$  (measured from the  $I = 0$   $g_3$  line) and that of the highest field line in the spectrum. Although we cannot give a good explanation for our inability to provide a fit to the high-field region at this time, this may well be due to a small quadrupole interaction from Pd. Assuming a 25 G splitting for  $A_3(\text{Pd})$ , the average of the three anisotropic splittings (32 G) is in reasonable agreement with the observed isotropic splitting (29 G) if it is assumed that all three splittings have the same sign.  $g$  values and hyperfine splittings (in  $\text{cm}^{-1}$ ) are collected in Table I.

The data of Table I have been used with eq 4-9 to calculate  $P$  and  $K$  values for this Pd(I) species, again assuming a  $B_{1g}$

ground state. The sign of each palladium splitting is required to be positive in order to yield the expected negative value for  $P$  for this nucleus (Pd has a negative  $g_N$ ). This analysis yields  $P = -26 \times 10^{-4} \text{ cm}^{-1}$  and  $K = 1.2$ . A free ion value of  $P_0 = -58 \times 10^{-4} \text{ cm}^{-1}$  has been calculated for Pd(I),<sup>16</sup> yielding a value of  $P/P_0 = 0.45$  for Pd(mnt)<sub>2</sub><sup>3-</sup>. Thus it would seem that considerably more in-plane covalency exists for the Pd(I) complex in comparison to the congeneric Ni(I) complex.

One interesting observation which can be made from these data is the rather large isotropic component to the palladium splittings, as reflected by the value of  $K$ , which is several times as large as that calculated for the nickel complex. Similar values of  $K$  for palladium have been found in Pd(acac)<sub>2</sub><sup>-20</sup> and PdCl<sub>4</sub><sup>3-16</sup> as well as for formally Pd(III) in Pd(mnt)<sub>2</sub><sup>-25</sup>. The question must be raised as to whether or not these high isotropic contributions can be traced to direct admixture of metal  $s$  and  $d$  orbitals which cannot occur in  $D_{2h}$  symmetry for a  $d_{xy}$  orbital but which could occur if the symmetry of the complex were sufficiently lowered by distortion. Such a direct-mixing process would, as shown by McGarvey,<sup>32</sup> lead to a *negative* contribution to  $K$  and is inconsistent with the large *positive* value of  $K$  observed experimentally, and so the  $s$ -orbital character to the Pd spin density must be due to a spin-polarization mechanism.

### Discussion

A wealth of data, including ESR, electronic spectroscopy, and molecular orbital calculations, are consistent with the orbital ordering of Scheme A, Figure 6, in square-planar dithiolene complexes with first-row transition metals.<sup>33,34</sup> In complexes of the type  $MS_4^-$  ( $M = \text{Ni, Pd, Pt}$ ), the  $3b_{2g}$  orbital is half-occupied and highly delocalized over the metal and ligand. These have sometimes been referred to as  $d^7$  complexes<sup>23,25,26</sup> although the heavy ligand contribution makes the oxidation state formalism less useful than ever, except for keeping track of electrons. The  $CuS_4^{2-}$ ,  $d^9$ , system has half-occupancy of the  $3b_{1g}$  orbital in which the metal contribution is an in-plane ( $d_{xy}$ ) orbital.<sup>23</sup> The  $MS_4^{3-}$  species made in this study ( $M = \text{Ni, Pd, Pt}$ ) are isoelectronic with the  $d^9$  Cu(II) complex and, as such, are expected to have a  $3b_{1g}$  ground state. As shown above, the results for the Ni and Pd complexes are consistent with this assumption, but even in the absence of ESR data, we are suspicious of this assumption for the platinum trianion, as discussed below.

**Pt(I).** It is not possible to explain the electrochemical behavior of the platinum complex on the basis of the same electronic structure as the nickel and palladium complexes. For an alternative explanation we turn to the data on Au(mnt)<sub>2</sub><sup>2-</sup> recently published by Schlupp and Maki.<sup>35</sup> These authors investigated, by dilute single-crystal ESR spectroscopy, the ground state of this formal  $d^9$ , Au(II), system which is isoelectronic with our Pt<sup>I</sup>(mnt)<sub>2</sub><sup>3-</sup>. They concluded that the ground state was different from that of the congeneric Cu(II) complex and that the ordering of the highest energy orbitals in the gold system is as shown in Figure 6, scheme B. In this case, the unpaired electron is in an  $A_g$  orbital which was calculated to be composed of about 80% *ligand* character, with the remainder of the spin being  $6s$  and  $5d$  metal in character. This scheme requires the  $B_{1g}$  orbital, normally half-filled in  $d^9$  dithiolene complexes, to be raised in energy above the  $A_g$  orbital. This result can be rationalized by the general observation that the metal  $d$  orbitals will be raised in energy in the heavier transition metals whereas the ligand-based orbitals should be relatively unaffected.<sup>36</sup>

It is probable, therefore, that the gold and platinum mnt complexes have similar electronic structures and that the electrochemical behavior of Pt(mnt)<sub>2</sub><sup>2-</sup> is related to this fact. Possibly, the  $B_{1g}$  and  $A_g$  orbitals are close in energy, leading to successive signal occupancy of each of these orbitals in the

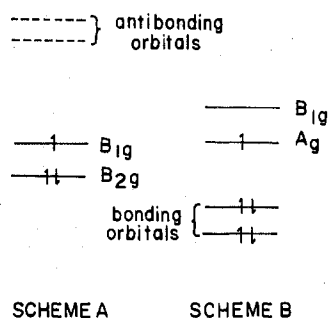


Figure 6. Proposed energy levels: scheme A,  $M(\text{mnt})_2^-$ ,  $M(\text{mnt})_2^{3-}$  ( $M = \text{Ni, Pd}$ ) and  $M(\text{mnt})_2^{2-}$  ( $M = \text{Cu}$ ); scheme B,  $\text{Au}(\text{mnt})_2^{2-}$ . Occupancy shown for  $d^9$  complexes.

sequence  $\text{Pt}(\text{mnt})_2^{2-} \rightarrow \text{Pt}(\text{mnt})_2^{3-} \rightarrow \text{Pt}(\text{mnt})_2^{4-}$ . Unless this question can be resolved, it is not possible to assign  $\text{Pt}(\text{mnt})_2^{3-}$  as a Pt(I) species, for the reduction of the Pt(II) complex could be either metal or ligand based.

**Ni(I), Pd(I).** In comparing the bonding parameters derived from our ESR study on Ni(I) and Pd(I) with those found by other workers<sup>16,20,23,37</sup> for  $d^9$  complexes, we note that in some other cases<sup>16,20,37</sup> a different method for calculation of the metal covalency was employed, specifically using eq 12 and 13 in

$$A_{\parallel} = -K + P_0[-(4/7)\alpha^2 + (g_{\parallel} - g_e) + (3/7)(g_{\perp} - g_e)] \quad (12)$$

$$A_{\perp} = -K + P_0[(2/7)\alpha^2 + (11/14)(g_{\perp} - g_e)] \quad (13)$$

which  $K$  gives the Fermi contact parameter in  $\text{cm}^{-1}$  and  $\alpha^2$  is a fraction related to the reduction of  $P_0$  from the free-ion value (that is,  $\alpha^2$  is the covalency factor). As a check on the analogy of these two approaches, we used our data on Pd(mnt)<sub>2</sub><sup>3-</sup> to calculate  $\alpha^2 = 0.50$  from eq 12 and 13 compared with  $P/P_0 = 0.45$  from eq 4-9. Thus these two methods yield at least a consistent picture of the metal-ligand spin density distribution, an observation made previously on  $d^7$  systems by Kalbacher and Bereman.<sup>38</sup> Literature data on  $d^9$  coordination compounds of Ni, Pd, and Cu are collected in Table II. It is possible to conclude on the basis of this very limited number of samples that for  $d^9$  complexes of a particular ligand, the amount of metal-ligand delocalization increases in the order  $\text{Ni} < \text{Pd} \approx \text{Cu}$ . It is quite clear that the calculated covalency for  $d^9$  Cu and Pd complexes of the dithiolate ligand is greater than that for the same metals with the bidentate oxygen chelate, acetylacetonate.

We cannot presently offer an explanation why the  $K$  values for Pd(I) complexes appear to be so much larger than those for Ni(I) or Cu(II). It is possible that this reflects a property of heavier transition metals with their much larger spin-orbit coupling constants, but theoretical calculations are not presently available to test this hypothesis.

The present study also affords the opportunity of measuring the metal/ligand spin distribution of two different orbitals in the same complex, since our data on the *trianions* of Ni(mnt)<sub>2</sub> and Pd(mnt)<sub>2</sub> can be compared with those acquired earlier by Maki and co-workers<sup>23-25</sup> on the *monoanions* of these same complexes. Some of these data are summarized in Table I. The contrast between the character of the two different half-occupied orbitals is obvious. The metal contribution to the  $B_{1g}$  orbitals in the  $d^9$  complexes appears to be two to four times that of the same metal in the  $B_{2g}$  orbitals of the  $d^7$  cases.

**Summary.** The electrochemical reduction of  $M[\text{S}_2\text{C}_2(\text{CN})_2]_2^{2-}$ ,  $M = \text{Ni, Pd, Pt}$ , yields air sensitive but otherwise stable  $d^9$ , M(I) species when  $M = \text{Ni, Pd}$ . Analyses of the metal hyperfine splittings in ESR spectra of frozen glasses of the Ni(I) and Pd(I) complexes are consistent with the unpaired electron occupying a  $3b_{1g}$  orbital, as found previously for the isoelectronic Cu(mnt)<sub>2</sub><sup>2-</sup> complex. The behavior of the Pt(mnt)<sub>2</sub><sup>2-</sup> complex provides evidence that a different ground

state may occur in the analogous  $\text{Pt}(\text{mnt})_2^{3-}$  species.

**Acknowledgment.** The authors are grateful to the National Science Foundation and Research Corp. for support of this work and to Dr. L. V. Interrante for providing the  $\text{M}[\text{S}_2\text{C}_2(\text{CF}_3)_2]_2$  samples. We also wish to acknowledge our appreciation of the generous loan of platinum and palladium salts from the Matthey Bishop Co.

**Registry No.**  $\text{Ni}(\text{mnt})_2^{3-}$ , 38117-63-4;  $\text{Pd}(\text{mnt})_2^{2-}$ , 19555-33-0;  $\text{Pd}(\text{mnt})_2^{3-}$ , 62906-14-3;  $\text{Pt}(\text{mnt})_2^{2-}$ , 15152-99-5;  $\text{Pt}(\text{mnt})_2^{3-}$ , 62906-13-2;  $\text{Pt}(\text{mnt})_2^{4-}$ , 62906-12-1.

## References and Notes

- (1) A. V. Kramer and J. A. Osborn, *J. Am. Chem. Soc.*, **96**, 7832 (1974).
- (2) J. M. Davidson and C. Triggs, *J. Chem. Soc. A*, 1324 (1968).
- (3) I. I. Moiseev and S. V. Pestrikov, *Dokl. Akad. Nauk SSSR, Ser. Khim.*, **171**, 722 (1966).
- (4) I. I. Moiseev and S. V. Pestrikov, *Dokl. Akad. Nauk SSSR, Ser. Khim., Engl. Transl.* **178**, 132 (1968).
- (5) D. Bingham and M. G. Burnett, *J. Chem. Soc. A*, 2165 (1970).
- (6) See D. J. Doonan, A. L. Balch, S. Z. Goldberg, R. Eisenberg, and J. S. Miller, *J. Am. Chem. Soc.*, **97**, 1961 (1975); J. Boehm, D. J. Doonan, and A. L. Balch, *ibid.*, **98**, 4845 (1976); M. F. Rettig, E. A. Kirk, and P. M. Maitlis, *J. Organomet. Chem.*, **111**, 113 (1976), and references therein.
- (7) T. E. Mines and W. E. Geiger, Jr., *Inorg. Chem.*, **12**, 1189 (1973).
- (8) W. E. Geiger, Jr., T. E. Mines, and F. C. Senftleber, *Inorg. Chem.*, **14**, 2141 (1975).
- (9) F. C. Senftleber and W. E. Geiger, Jr., *J. Am. Chem. Soc.*, **97**, 5018 (1975).
- (10) See ref 8, and citations therein, for a summary of Ni(I) complexes reported through 1974.
- (11) F. V. Lovecchio, E. S. Gore, and D. H. Busch, *J. Am. Chem. Soc.*, **96**, 3109 (1974).
- (12) S. C. Jain, K. V. Reddy, C. L. Gupta, and T. R. Reddy, *Chem. Phys. Lett.*, **21**, 150 (1973).
- (13) T. Feldmann, A. Treninen, and V. Volterra, *J. Chem. Phys.*, **42**, 3366 (1965).
- (14) U. Kaufmann, *Phys. Rev. B*, **11**, 2478 (1975).
- (15) R. K. Watts, *Phys. Rev.*, **188**, 568 (1969).
- (16) T. Krigas and M. T. Rogers, *J. Chem. Phys.*, **54**, 4769 (1971).
- (17) S. Fujiwara and M. Nakamura, *J. Chem. Phys.*, **52**, 6299 (1970).
- (18) S. Fujiwara and M. Nakamura, *J. Chem. Phys.*, **54**, 3378 (1971).
- (19) M. Nakamura and S. Fujiwara, *J. Coord. Chem.*, **1**, 221 (1971).
- (20) M. Nakamura and S. Fujiwara, *J. Phys. Chem.*, **78**, 2136 (1974).
- (21) T. Krigas and M. T. Rogers, *J. Chem. Phys.*, **55**, 3035 (1971).
- (22) R. S. Eachus and R. E. Graves, *J. Chem. Phys.*, **63**, 83 (1975).
- (23) A. H. Maki, N. Edelstein, A. Davison, and R. H. Holm, *J. Am. Chem. Soc.*, **86**, 4580 (1964).
- (24) R. D. Schmitt and A. H. Maki, *J. Am. Chem. Soc.*, **90**, 2288 (1968).
- (25) R. L. Schlupp, Ph.D. Thesis, University of California at Riverside, 1973.
- (26) R. Kirmse and W. Dietzsch, *J. Inorg. Nucl. Chem.*, **38**, 255 (1976).
- (27) A. Davison and R. H. Hohn, *Inorg. Synth.*, **10**, 19 (1967).
- (28) A. H. Maki and D. H. Geske, *J. Chem. Phys.*, **30**, 1356 (1959).
- (29) M. J. Hove, B. M. Hoffman, and R. J. Loyd, *J. Phys. Chem.*, **76**, 1849 (1972).
- (30) C. K. Mann and K. K. Barnes, "Electrochemical Reactions in Nonaqueous Systems," Marcel Dekker, New York, N.Y., 1970, Chapter 10.
- (31) A. Abragam, J. Horowitz, and M. H. L. Pryce, *Proc. R. Soc. London, Ser. A*, **230**, 169 (1955).
- (32) B. R. McGarvey, *J. Phys. Chem.*, **71**, 51 (1967).
- (33) Reviewed in J. A. McCleverty, *Prog. Inorg. Chem.*, **10**, 49 (1968).
- (34) G. N. Schrauzer, *Acc. Chem. Res.*, **2**, 72 (1969).
- (35) R. L. Schlupp and A. H. Maki, *Inorg. Chem.*, **13**, 44 (1974).
- (36) A cautionary note must be injected here, for another ESR study on  $\text{Au}(\text{mnt})_2^{2-}$  [J. G. M. Van Rens, M. P. A. Vieggers, and E. De Boer, *Chem. Phys. Lett.*, **28**, 104 (1974)] has appeared which argues with Schlupp and Maki concerning the ground state of the  $\text{Au}(\text{mnt})_2^{2-}$  complex.
- (37) A. H. Maki and B. R. McGarvey, *J. Chem. Phys.*, **29**, 31 (1958).
- (38) B. J. Kalbacher and R. D. Bereman, *Inorg. Chem.*, **12**, 2997 (1973).

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## An Angular Overlap Treatment of $\sigma$ and $\pi$ Bonding in f-Orbital Compounds

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Received January 31, 1977

AIC70053E

By use of the recently published f-orbital angular transformation matrix, the angular overlap treatment is extended to embrace both  $\sigma$  and  $\pi$  (and higher  $\lambda$ ) interactions in f-orbital compounds. Results are listed for a number of geometries, especially those commonly encountered in 4f and 5f complexes, and applied in particular to the estimation of the relative contributions of  $\sigma$  and  $\pi$  interactions in octahedral hexahalo species.

### Introduction

The angular overlap model, first propounded by Jorgensen, Pappalardo, and Schmidtke,<sup>1</sup> was originally introduced in an attempt to understand the small 4f ligand field splittings observed for various complexes of the lanthanide series. Thus, it was argued, considering only  $\sigma$ -bonding effects, that such splittings were better interpreted in terms of a number of one-electron f-orbital energies (depending upon a single parameter characteristic of the ligands), rather than by use of a symmetry-determined number of  $A_{\lambda}^k(r^k)$  parameters, arising from the electrostatic treatment. Subsequently, by use of the equivalent singular-contact potential method, this approach was extended to include also the effects of  $\pi$ -bonding interactions,<sup>2</sup> but the necessary general angular transformation matrices required were given only for the cases  $l = 1$  and  $l = 2$ , the results listed being restricted to p- and d-orbital systems. Thereafter, although reference has been made<sup>3</sup> to the existence of the required f-orbital transform, the results for the case  $l = 3$  have only recently become generally available, as given by Clack and Smith.<sup>4</sup>

Consequently it is now possible to consider via the angular overlap model the effects of  $\pi$  bonding (and in principle the higher  $\lambda$  interactions of  $\delta$  and  $\phi$  symmetry) for f-orbital systems as well to treat  $\sigma$  interactions not previously investigated, and the results are now given for a variety of geometric arrangements known to occur in the 4f and 5f series. These

include systems containing two-nine ligands, and examples belong to the point groups  $D_{\infty h}$ ,  $D_{3h}$ ,  $D_{4h}$ ,  $D_{5h}$ ,  $D_{6h}$ ,  $T_d$ , and  $O_h$ . In general the results are confined to  $\text{ML}_N$  systems with all  $N$  ligands equivalent, but possible extensions to nonequivalent situations are noted in some instances.

### Theory

The theory of the angular overlap model<sup>1-3</sup> has recently been succinctly summarized by Gerloch and Slade,<sup>5</sup> and only a brief outline of its conclusions is now therefore given. Thus one considers a chromophore,  $\text{ML}_N$ , where  $N$  is the number of coordinated ligands ( $L$ ),  $l$  is the azimuthal quantum number for the orbitals of the metal ( $M$ ) under consideration, and  $\lambda$  denotes the component of the angular momentum of any given molecular orbital about the internuclear axis (for  $\lambda = 0, 1, 2, 3, \dots$  one has respectively  $\sigma, \pi, \delta, \phi, \dots$  interactions). Assuming that the ligand orbitals lie energetically below those of the metal and that all the ligands are equivalent with no ligand  $\lambda$  orbital interacting with two nondegenerate metal orbitals, the antibonding energies of the metal  $l$  orbitals may be written as

$$E^* = e_{\lambda} \sum_{j=1}^N (F_{\lambda}^j)^2$$

where the  $e_{\lambda}$  quantities depend only on the radial functions of the metal and of the ligands and on the bond distance and