The Conductivities of Some Transition-metal Dithiolates and other Complexes, Their Dependences on Cation Properties, and the Role of Anion Disproportionation

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The dependences of the conductivities, and their associated activation energies, for three maleonitriledithiolate anions, with Ni or Fe centres, have been studied in relation to the size and redox tendencies of the cations. Phenyl-containing cations and Methylene Blue allow higher conductivities than would be predicted from their radii, largely because of their redox (donor or acceptor) capacities. Sandwich compounds have low conductivities, presumably arising from their predominantly intra- rather than inter-molecular interactions. Comparison of the conductivities of two substances, differing essentially only in the charge of an ion, shows them to be related to the ease of disproportionation of the ions acting as transfer centres.

THE currently increasing interest in solid-state conductivities is establishing detailed mechanisms for the molecular charge-transfer events, using on the one hand the conduction band, polaron,[1] and hopping-electron [2] models from physics and on the other the chemical redox properties of the participating electron-transfer centres.[3] As a group of compounds of widely varying conductivity, the dithiolates are of particular interest.[4] The high conductivity of the best-conducting adduct,[5] $[Ni(mnt)_2]$–perylene, was considered to involve transfer between the perylene donor molecules in stacked arrays (mnt = maleonitriledithiolate). Since then the compounds $[M][Ni(mnt)_2]$ ($M = [NH_4]^+$ or other singly charged cations) have been shown [6] to conduct by anion-to-anion transfer: in view of the extensive range [7] of (apparent) metal-ion oxidation states in isostructural complexes, this was to be expected. There is furthermore no reason to discount donor–acceptor–donor (*i.e.* anion–cation–anion) electron-transfer paths as well, and it has been inferred [3] that a redox-active donor such as Methylene Blue (mb) is as effective in enhancing conductivity as is a mixture of dithiolate anions of differing oxidation states which facilitates ' inter-valence ' anion–anion transfer. Wider studies of pure dithiolates are reported here, in an attempt to throw more light on the relative importance of donor–donor (or acceptor–acceptor) routes in competition with the donor–acceptor–donor path.

A major factor governing the conductivity is the extent of orbital overlap between the transfer centres,[8] itself critically dependent on the separation of these centres; in the highly conducting ttf–tcnq series [9] (tcnq = tetracyanoquinodimethane, ttf = tetrathiafulvalene), the insertion of bulky substituents diminishes the conductivity markedly.[10] While the stacking ability of planar aromatic cations is suggested [11] to be conducive to high conductivity, their redox (donor or acceptor) propensity should also be relevant. In contrast to the dithiolates, a few differing structures including some of the sandwich type have been examined. Preliminary values of some of the present results have been reported.[12]

EXPERIMENTAL

Preparations followed the literature references in Table 1 or, when new, were adaptations of literature procedures (see below). Elemental analyses were satisfactory, and i.r. spectra conformed with reports when available. Detailed preparations are given because of the occasional sensitivity of κ to the method of preparation.

$Na_2[Fe(mnt)_3]$.—Iron(III) chloride hexahydrate (0.9 mmol) in water (2 cm^3) was added to a solution [13] of $Na_2[mnt]$ (2.7 mmol) in water (2 cm^3), giving a brown-black deposit, which on filtration and vacuum-drying (80 °C) gave a black amorphous powder.

$[mb]_2[Fe(mnt)_3]$.—The compound $FeCl_3\cdot6H_2O$ (0.9 mmol) in dimethylformamide (dmf) (2 cm^3) when added to $Na_2[mnt]$ (2.7 mmol) in dmf–MeOH (50%; 20 cm^3) gave a brown solution to which, after heating on a steam-bath, the addition of 1.8 mmol [mb]Cl in dmf–water (50%; 30 cm^3) resulted in a precipitate. After boiling, then cooling to 0 °C, blue-violet microcrystals were filtered off and dried. A similar product was obtained from acetone in place of dmf, but water as sole solvent gave a highly erratic irreproducible product.

The compound $[thi]_2(Fe(mnt)_3]$ (thi = thionine) was prepared as for $[mb]_2[Fe(mnt)_3]$, but using thi, as a purple deposit which formed dark blue granules. Grinding and final drying (60 °C, 1 h) gave a dark blue-brown powder.

$[mb]_2[\{Fe(mnt)_2\}_2]$.—To $Na_2[mnt]$ (1 mmol) in boiling EtOH (3.5 cm^3) was added $FeCl_3\cdot6H_2O$ (0.5 mmol) in hot EtOH (2 cm^3), the solution was filtered, and 0.5 mmol [mb]Cl in MeOH (5 cm^3) added. The black precipitate obtained on cooling was recrystallised from dmf–dmso (dmso = dimethyl sulphoxide) and dried.

$[mb][Ni(mnt)_2]$.—A boiling solution of $Na_2[mnt]$ (4 mmol) in EtOH (16 cm^3) was added to $NiCl_2\cdot6H_2O$ (2 mmol) in EtOH–water (50%, 16 cm^3), the solution was filtered, and then added to I_2 (5 mmol) in EtOH (20 cm^3). The product was precipitated on addition of [mb]Cl (2 mmol) in methanol (24 cm^3), washed (water, EtOH, diethyl ether), and recrystallised (dmf). The preparation of $[PMePh_3][Ni(mnt)_2]$ was similar. The compounds $[PPh_4]_2[Ni(mnt)_2]$ and $[mb]_2[Ni(mnt)_2]$ were obtained as in ref. 13.

$[Fe(tcnq)(C_6Me_6)_2]$ (C_6Me_6 = *Hexamethylbenzene*).[14]—The compound Li[tcnq] in acetone (25 cm^3) was added to $[Fe(C_6Me_6)_2][PF_6]_2$ (0.05 mmol) in acetone (10 cm^3) (both boiling). The dark purple microcrystals formed were washed then dried at 60 °C. They were sparingly soluble in dmf and dmso.

[mb][tcnq]. The compound Li[tcnq] [15] in EtOH (10 cm^3) was added to an equimolar amount of [mb]Cl. The brown deposit, on filtration, washing with EtOH and diethyl ether, and drying, gave a purple amorphous powder.

B.D.H. [mb]Cl was used, tcnq was from Aldrich, and the other reagents were AnalaR grade.

Where brittle, the samples were milled in a stainless-steel phial for 30 s, on a Glen Creston Wig/L/Bug ball mill, or, if soft, ground for 2 min by hand with an agate pestle and mortar. Samples were outgassed for 1—2 h and compacted at 10 tons [*] for 3 min (this pressure giving pressure-independent conductivities for these and other [16] solids). The discs were of 13 mm diameter and 0.25—0.75 mm thickness. D.c. conductivities were calculated from the current on a Keithley 610C electrometer, with a potential V across the sample. From 1 to 100 V the currents were ohmic or slightly superohmic ($V^{1.0}$ to $V^{1.3}$) but a 1.6 exponent of V was shown for $[Fe(C_6Me_6)_2][PF_6]_2$ and $Na_2[Fe(mnt)_3]$. Values at 10 V are given, this being sufficient to yield measurable currents, while minimising non-ohmic components. Activation energies were satisfactorily reproducible for different preparations, to within ± 2 kJ mol^{-1}, except for $[mb]_2[Fe(mnt)_3]$ precipitated from water, as noted above. Polarities were always reversed, and temperatures were both increased and decreased in measurements of $E^‡$ to check the reproducibility. Three kinds of contact were used: (*a*) silver paint to copper leads attached to Perspex rod supports [these could be immersed in light petroleum (shown to be quite inert) in a boiling tube itself immersed in a Dewar flask containing appropriate freezing mixtures]; (*b*) mercury contacts in a specially designed cell; [17] and (*c*) platinum discs under a low pressure in a vacuum brass cell.[17] For the higher temperatures the third cell was suspended in an oven. Except for gross deviations when occasionally the material dissolved in the silver-paint solvent (isopropyl methyl ketone), the reproducibility of κ for any one sample was within 10—20%, while values for replica samples agreed within a factor of three or four, which was entirely satisfactory [18] in view of the many orders of magnitude studied.

RESULTS AND DISCUSSION

The results are presented in Table 1. It has been shown [18-20] that compressed discs serve well as approximations to single crystals (and are the only accessible form in cases where amorphous powders are the sole product of preparations). This generalisation is less true for anisotropic materials when the lowest-conductivity component will predominate.[21] The results are best considered under two main headings: (*i*) anion kept constant but cation changed, for the effect of cationic structure and properties; and (*ii*) cation kept constant (in kind not number) with anion constant (in kind but not charge).

(*i*) *Effect of Cations*.—This is illustrated in Table 2. Only the structure of $[PPh_3][Ni(mnt)_2]$ is known,[22] in which anions and cations form separate columns running through the structure. The salt [†] $[tmpd]_2[Ni(mnt)_2]$ has [23] juxtaposed cation pairs and planar sheets of anions, while $[NMe_4]_2[Ni(mnt)_2]$ has [24] alternating anion–cation sequences; other geometries have been found [25-27] with other cations. Nevertheless, cationic radii can be assigned as the best available structural parameters.

TABLE 1

Conductivity κ, activation energy $E^‡$, and the range of temperature θ_c used in the measurement of $E^‡$

Compound	κ at 25 °C / S cm^{-1}	$E^‡$ / kJ mol^{-1}	θ_c range / °C
$[PPh_4]_2[Fe(mnt)_3]$ [a]	3×10^{-11}	90	0/60
$Na_2[Fe(mnt)_3]$	10^{-5}	58	−64/21
$[mb]_2[Fe(mnt)_3]$	2×10^{-6}	22	−78/25
$[thi]_2[Fe(mnt)_3]$	2×10^{-8}	20	−75/21
$[NEt_4]_2[Ni(mnt)_2]$ [b]	2×10^{-12}	67	22/92
$[NBu_4]_2[Ni(mnt)_2]$ [13]	5×10^{-13}	135	25/80
$[PPh_4]_2[Ni(mnt)_2]$ [c]	5×10^{-9}	37	−42/19
$[mb]_2[Ni(mnt)_2]$	10^{-9}	40	−78/25
$[NEt_4][Ni(mnt)_2]$ [d]	5×10^{-9}	29	−60/59
$[NBu_4][Ni(mnt)_2]$ [13]	7×10^{-13}	125	21/85
$[NMe_4][Ni(mnt)_2]$ [13]	3×10^{-9}	29	22/80
$[PMePh_3][Ni(mnt)]$	4×10^{-10}	31	22/81
$Na[Ni(mnt)_2]$ [e]	2×10^{-6} [f]	(30)	−75/18
$[mb][Ni(mnt)_2]$	6×10^{-7}	27	−75/18
$[mb]_2[\{Fe(mnt)_2\}_2]$	2×10^{-11}	52	−43/50
$[Fe(tcnq)_2(C_6Me_6)_2]$	3×10^{-9}	43	−65/55
$[Fe(C_6Me_6)_2][PF_6]_2\cdot an$ [g, h]	10^{-10}	70	−20/90
$[Fe(C_6Me_6)_2][PF_6]_2\cdot[Fe(C_5H_5)_2]$ [g]	4×10^{-10}	69	−20/90
$[mb][tcnq]$	2×10^{-6}	23	−75/20
$[mb]Cl$	*ca.* 10^{-6}		25

[a] J. A. McCleverty, J. Locke, E. J. Wharton, and M. Gerloch, *J. Chem. Soc.* (*A*), 1968, 816. [b] E. Billig, R. Williams, I. Bernal, J. H. Waters, and H. G. Gray, *Inorg. Chem.*, 1964, **3**, 663. [c] By modification of a method in ref. 13. [d] A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, *Inorg. Chem.*, 1963, **2**, 1227. [e] J. F. Weiher, L. R. Melby, and R. E. Benson, *J. Amer. Chem. Soc.*, 1964, **86**, 4329. [f] Different values have been cited (see text). [g] J. F. Holling and D. M. Braitsch, *J. Amer. Chem. Soc.*, 1970, **92**, 7207. [h] an = Anthracene.

TABLE 2

Dependence of conductivity κ of dithiolates on cation and cationic radius

Cation	Radius/Å	κ/S cm^{-1} $[Fe(mnt)_3]^{2-}$	κ/S cm^{-1} $[Ni(mnt)_2]^{2-}$	κ/S cm^{-1} $[Ni(mnt)_2]^{-}$
$[PPh_4]^+$	6,[a] 4.2 [b]	3×10^{-11}	5×10^{-9}	
$[PMePh_3]^+$	5.4 [b, c]			4×10^{-10}
$[NBu_4]^+$	5.0 [c]		5×10^{-13}	7×10^{-13}
$[NEt_4]^+$	4.0 [c]		2×10^{-12}	5×10^{-9}
$[NMe_4]^+$	3.5 [c]		2×10^{-11} [d]	3×10^{-9}
$[mb]^+$	1.7 [e]	2×10^{-6}	10^{-9}	6×10^{-7} (2×10^{-6})
$[Na]^+$	0.9	1×10^{-5}		

[a] C. J. Fritchie, jun., *Acta Cryst.*, 1966, **B20**, 107. [b] From the Stokes law using the molar conductivity from A. Fidler and J. Vretal, *Coll. Czech. Chem. Comm.*, 1970, **35**, 1905. [c] R. A. Robinson and R. H. Stokes, 'Electrolyte Solutions,' Butterworths, London, 1959, p. 125. [d] G. Manecke and D. Wohrle, *Makromol. Chem.*, 1968, **116**, 36. [e] A. Kahn-Harari, R. E. Ballard, and E. K. Norris, *Acta Cryst.*, 1973, **B29**, 1124. [f] See text.

Since the separation between anions will in general be determined largely by the size of the cations independently of structure, it is of interest to see whether this is reflected in the conductivities as would be expected for anion-to-anion charge transfer in the presence of inert cations. An overall upward trend of conductivities is discernible with decrease of cationic radii, which accords with the expectation of increasing orbital overlap between transfer centres. The radii are approximate estimates (note $[PPh_4]^+$) and the dimension for $[mb]^+$ is half the cation–cation separation in [mb][SCN], *i.e.* half the ' thickness ' of this planar molecule. While this

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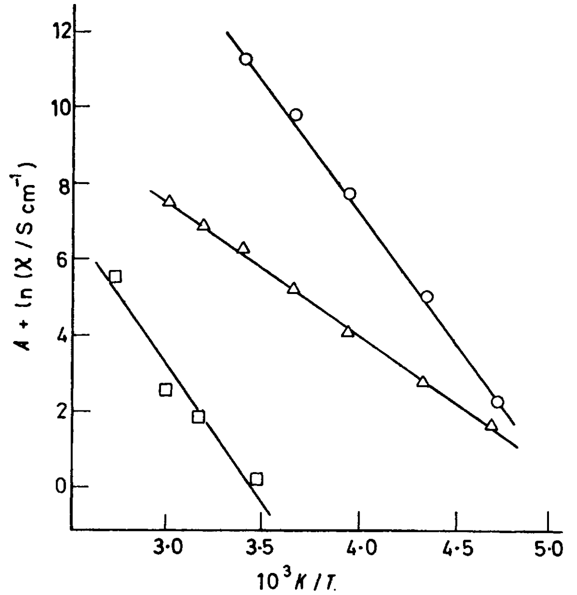
[*] Throughout this paper: 1 ton (U.K.) ≈ 1 Mg. κ is used for conductivity (elsewhere usually σ) and is expressed in Siemens per centimetre (usually Ω^{-1} cm^{-1}).

[†] tmpd is tetramethylphenylenediamine.

planarity may increase the conductivity because of closer anionic juxtaposition, the enhancement effect has been attributed [3] to charge transfer with the redox-active cation. Similarly, non-conforming (higher) conductivities are observed for cations partly comprising Ph groups, which again are intrinsically more charge-transfer-interactive than alkyls. Thus two cationic properties, size and charge-transfer propensity, nicely account for the observations.



Activation-energy plots for (○) $Na_2[Fe(mnt)_3]$ (A = 12), (△) $[NEt_4][Ni(mnt)_3]$ (A = 11), and (□) $[NEt_4]_2[Ni(mnt)_2]$ (A = 12)

The dimerised structure with $[\{Fe(mnt)_2\}_2]^{2-}$ is 3 × 10^4-fold less conducting than the corresponding $[Ni(mnt)_2]^-$. The Fe–Fe separation (*ca.* 6 Å) [2] indicates a strong intramolecular interaction presumably at the expense of intermolecular or anion–cation contact, and therefore of conductivity, as has been observed for neutral (uncharged) dithiolates.[28] The non-dithiolate transition-metal complexes all exhibit low conductivity again because of the dominance of intra- over intermolecular interaction. The compound [mb][tcnq] is among the more highly conducting in this group, as might have been expected from the components, but the conductivity is nevertheless not high, being of the same order as that of [mb]Cl.

The activation energies (Figure) do not reveal any irregularities or qualifications of the foregoing, in that the sequence closely follows that of κ at 25 °C. It is useful to note that they span the usual range found for solution-phase electron-transfer reactions, *ca.* 16 to two or three hundred kJ mol^{-1}.

(*ii*) *Effect of Anionic Charge*.—Table 2 illustrates that $[Ni(mnt)_2]^-$ compounds are more highly conducting than $[Ni(mnt)_2]^{2-}$. For uncharged dithiolates of Ni, Pt, and Pd it has been shown [20] that the conductivities follow the half-wave potentials $E_{\frac{1}{2}}(0, -1)$ for dithiolate(0) + $e^- \longrightarrow$ dithiolate(1−). It is not clear how the correlation arises, since in the conducting solid the source of e would be another neutral dithiolate(0), by the reaction dithiolate(0) $\longrightarrow$ dithiolate(1+) + e^-. The net process is thus 2 dithiolate(0) $\longrightarrow$ dithiolate(1−) + dithiolate(1+). Therefore it is expected that $\Delta E_{\frac{1}{2}}$ values for such disproportionations will determine the relative conductivities, where $\Delta E_{\frac{1}{2}} = E_{\frac{1}{2}}(0,-1) - E_{\frac{1}{2}}(+1,0)$. The latter values are not available, but if, as is likely, the relevant successive $E_{\frac{1}{2}}$ values for a particular structure are monotonously related, then the correlation [20] could follow. For the nickel dithiolates in the present study the two disproportionations are (1) and (2). In this case

$$2[Ni(mnt)_2]^- \longrightarrow [Ni(mnt)_2] + [Ni(mnt)_2]^{2-} \quad (1)$$

$$2[Ni(mnt)_2]^{2-} \longrightarrow [Ni(mnt)_2]^- + [Ni(mnt)_2]^{3-} \quad (2)$$

the three $E_{\frac{1}{2}}$ values *are* available (Table 3) and give the $\Delta E_{\frac{1}{2}}$ values for both disproportionations. These are respectively −0.79 and −1.91 V, greatly favouring reaction (1), and so indicating the higher conductivity of the $[Ni(mnt)_2]^-$ complexes, as is observed. Since lattice energies and other interactions will in general be greater for 2− than 1− ions, correspondingly greater contributions to the electron-transfer activation energy will arise. Therefore we compare $\Delta E_{\frac{1}{2}}$ for $[Fe(mnt)_3]^{2-}$ with that for $[Ni(mnt)_2]^{2-}$, qualified now by the change of core and anionic size, to obtain −0.99 *cf.* −1.91 V, respectively, again parallel with the observed magnitudes

TABLE 3

Conductivities κ and ΔE values for disproportionation

Ion 1	ΔE/V	Ion 2	ΔE/V	Predicted relative conductivity	$\kappa_{obs.}$/S cm^{-1}	
					κ_1	κ_2
$[Ni(mnt)_2]^{2-}$	−1.9 [a]	$[Ni(mnt)_2]^-$	−0.8 [a]	$\kappa_2 > \kappa_1$	10^{-12} [b]	10^{-8} [b]
$[MnO_4]^{2-}$	−0.3 [c]	$[MnO_4]^-$	*h*	$\kappa_1 > \kappa_2$	*ca.* 5 × 10^{-8} [d]	*ca.* 10^{-10} [d]
Vanadate(III)	−0.6 [c]	vanadate(IV)	−0.6 [c]	$\kappa_1 \approx \kappa_2$	Extrapolated [e] $\kappa_1 \approx \kappa_2 \approx$	
Manganate(III)	−0.1 [f]	manganate(IV)	−2.1 [f]	$\kappa_1 > \kappa_2$	Extrapolated [e] $\kappa_1 > \kappa_2$	
$CuCl_2$	−2.1 [c]	CuCl	+0.1 [c]	$\kappa_2 > \kappa_1$	10^{-11} [g]	10^{-9} [i]

The ΔE are the $E^{\ominus}$ values for the disproportionations, or the $\Delta E_{\frac{1}{2}}$ values when $E^{\ominus}$ values are lacking.

[a] W. E. Geiger, T. E. Mines, and F. C. Sentleber, *Inorg. Chem.*, 1975, **14**, 2141. [b] Ref. 3. [c] L. G. Sillén and A. E. Martell, ' Stability Constants of Metal–Ion Complexes,' *Special Publ.*, The Chemical Society, London, 1964, no. 17. [d] Ref. 17. [e] P. Day, *Endeavour*, 1970, **29**, 45. [f] D. R. Rosseinsky and M. J. Nicol, *Trans. Faraday Soc.*, 1965, **61**, 2718. [g] Anionic conductivity only, *i.e.* disproportionation does not contribute to κ; W. Jander, *Angew. Chem.*, 1929, **42**, 462. [h] Large and negative; $[MnO_4]^-$ simply does not disproportionate. [i] R. S. Bradley and D. C. Munro, *Trans. Faraday Soc.*, 1969, **65**, 1912.

of the conductivities. (Signs follow the Stockholm convention and $\Delta G^{\ominus} = -nF\Delta E_{\frac{1}{2}}$, where n is the number of electrons transferred and F the Faraday constant.)

In support, further examples of disproportionation mechanisms were sought, for pairs of salts differing only in charge of one of the ions, and for which all the $E_{\frac{1}{2}}$ or $E^{\ominus}$ values (obtained in the same solvent) for the two disproportionations were available. These are listed in Table 3, and in all cases the relative conductivities for each pair of solids follow the predictions from the relative ΔE values. The solution-phase data clearly provide valuable pointers to electron-transfer propensities in the solid state, and the disproportionation hypothesis is quite well supported for solids of widely differing type. For the dithiolates, the earlier explanation[28] for the correlation of $E_{\frac{1}{2}}$ with κ tentatively invoked an injection-controlled mechanism, which should have been non-ohmic, in conflict with observations.[28]

The κ value for $Na[Ni(mnt)_2]$ is in some doubt. A recent value[6] of 2×10^{-9} S cm^{-1} has been ascribed to incorporation of trace amounts of water, although a considerably higher value (2×10^{-4} S cm^{-1}), closer to ours, was obtained from a preparation not claimed to be especially anhydrous.[29] It is clear that substantial further work would be required to sustain the implication of water as being solely responsible, and we tentatively assume a value in the range of 10^{-6}—10^{-4} as being representative. {Indeed, we have found[12] that $[mb]_2[Fe(mnt)_3]$ precipitated from water has a very low conductivity relative to other samples.}

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REFERENCES

[1] N. F. Mott and R. W. Gurney, ' Electronic Processes in Ionic Crystals,' 2nd edn., Dover, New York, 1964, p. 86.

[2] R. R. Heikes and W. D. Johnston, *J. Chem. Phys.*, 1957, **26**, 582.

[3] D. R. Rosseinsky and R. E. Malpas, *J.C.S. Chem. Comm.*, 1977, 455.

[4] J. S. Miller and A. J. Epstein, *Progr. Inorg. Chem.*, 1976, **20**, 106.

[5] L. Alcacer and A. H. Maki, *J. Phys. Chem.*, 1974, **78**, 215.

[6] E. A. Perez-Albuerne, L. C. Issett, and R. K. Haller, *J.C.S. Chem. Comm.*, 1977, 417.

[7] J. A. McCleverty, *Progr. Inorg. Chem.*, 1968, **10**, 49.

[8] B. Mayoh and P. Day, *J. Amer. Chem. Soc.*, 1972, **94**, 2885.

[9] J. Perlstein, *Angew. Chem.*, 1977, **16**, 519.

[10] H. Kuakawa and K. Akashi, *Bull. Chem. Soc. Japan*, 1969, **42**, 263.

[11] K. W. Browall and L. V. Interrante, *J. Co-ordination Chem.*, 1973, **3**, 27.

[12] D. R. Rosseinsky, K. Kite, R. E. Malpas, and R. A. Hann, *J. Electroanalyt. Chem.*, 1976, **69**, 120.

[13] A. Davidson and R. H. Holm, *Inorg. Synth.*, 1967, **10**, 8.

[14] D. M. Braitsch, *J.C.S. Chem. Comm.*, 1974, 461.

[15] L. R. Melby, R. J. Harder, W. R. Hertler, W. Mahler, R. E. Benson, and W. E. Mochel, *J. Amer. Chem. Soc.*, 1962, **84**, 3374.

[16] F. Gutmann and L. E. Lyons, ' Organic Semiconductors,' J. Wiley, London, 1967, p. 168.

[17] D. R. Rosseinsky, R. E. Malpas, and T. E. Booty, *J. Phys.* (*E*), 1977, **10**, 1236.

[18] R. C. Wheland, *J. Amer. Chem. Soc.*, 1976, **98**, 3926.

[19] K. Schulgasser, *J. Appl. Phys.*, 1976, **47**, 1880.

[20] E. J. Rosa and G. N. Schrauzer, *J. Phys. Chem.*, 1969, **73**, 3132.

[21] C. M. Huggins and A. H. Sharbaugh, *J. Chem. Phys.*, 1963, **38**, 393.

[22] C. J. Fritchie, jun., *Acta Cryst.*, 1977, **20**, 107.

[23] M. J. Hove, B. M. Hoffmann, and J. A. Ibers, *J. Chem. Phys.*, 1972, **56**, 3490.

[24] R. Eisenberg, J. A. Ibers, R. J. H. Clark, and H. B. Gray, *J. Amer. Chem. Soc.*, 1964, **86**, 113; R. Eisenberg and J. A. Ibers, *Inorg. Chem.*, 1965, **4**, 605.

[25] I. G. Dance, P. J. Solstad, and J. C. Calabrese, *Inorg. Chem.*, 1973, **12**, 2161.

[26] D. Coucouvanis, N. C. Baenziger, and S. M. Johnson, *Inorg. Chem.*, 1974, **13**, 1191.

[27] J. S. Kasper, L. V. Interrante, and C. A. Secaur, *J. Amer. Chem. Soc.*, 1975, **97**, 890.

[28] Ref. 20, p. 3137.

[29] F. Wudl, C. H. Ho, and A. Nagel, *J.C.S. Chem. Comm.*, 1973, 923.