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Synthesis and Characterization of Tris(maleonitriledithiolato)metalates

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Complexes of the type $[(C_6H_5)_4As]_2[M(mnt)_3]$ ($mnt = \text{maleonitriledithiolate}$; $M = \text{Ti, V, Cr, Mn, Fe, Mo, W, Re}$) and $[(C_6H_5)_4As]_3[M(mnt)_3]$ ($M = \text{Cr, Co}$) have been prepared and characterized. X-Ray powder patterns, magnetic susceptibilities, electronic spectra, and polarographic results are reported. These data are shown to be consistent with the assignment of an octahedral structure to the trianionic complexes $\text{Cr}(mnt)_3^{3-}$ and $\text{Co}(mnt)_3^{3-}$ and the dianionic complexes $\text{Mn}(mnt)_3^{2-}$ and $\text{Fe}(mnt)_3^{2-}$. The distorted structure found for $\text{V}(mnt)_3^{2-}$ is probably also adopted by the $\text{Ti}(mnt)_3^{2-}$ and $\text{Cr}(mnt)_3^{2-}$ complexes. The assignment of geometry to the dianionic complexes of the second- and third-row metals is still in doubt, and the possibility of trigonal-prismatic coordination cannot be eliminated.

Introduction

There has been considerable interest of late in the six-coordinate complexes formed by bidentate, sulfurdonor ligands. Of particular significance has been the discovery that trigonal-prismatic as well as octahedral coordination can occur for these complexes. Thus X-ray structural studies on $\text{Re}(S_2C_2(C_6H_5)_2)_3$,² $\text{Mo}(S_2C_2H_2)_3$,³ and $\text{V}(S_2C_2C_6H_5)_3$ ^{4,5} and spectroscopic studies^{4,6,7} on neutral complexes of V, Cr, Mo, W, and Re with various 1,2-dithiolate⁸⁻¹⁰ ligands establish trigonal-prismatic coordination for these species. Additionally, spectroscopic studies⁴ of $\text{V}(S_2C_2(C_6H_5)_2)_3^-$ indicate that trigonal-prismatic coordination may be present in monoanionic species as well. Recently, some progress has been made toward structural elucidation of dianionic species. For example, $\text{V}(mnt)_3^{2-}$ has been found¹¹ in its $(CH_3)_4N^+$ salt to have a severely distorted structure between octahedral and trigonal-prismatic limits. Furthermore, $\text{Fe}(mnt)_3^{2-}$ in a $(C_6H_5)_4As^+$ salt has been found¹² to have an essentially octahedral structure.

In order to extend structural assignments to other dianionic and trianionic complexes, we have investigated the large series of complexes $[(C_6H_5)_4As]_2[M(mnt)_3]$ ($mnt = \text{maleonitriledithiolate}$) with $M = \text{Ti, V, Cr, Mn, Fe, Mo, W, and Re}$ and $[(C_6H_5)_4As]_3[M(mnt)_3]$ with $M = \text{Cr and Co}$. The V and Cr complexes were previously prepared by Davison and coworkers,¹³

whereas McCleverty and coworkers^{14,15} have reported additional results on complexes of Mn, Fe, Mo, and W with different cations. Where comparable, our results do not differ appreciably. In this paper we report synthetic details, X-ray powder patterns, magnetic susceptibilities, electronic spectra, and polarographic results. Our present data, coupled with results from the aforementioned studies, are used to infer structural patterns adopted by the dianionic and trianionic complexes.

Experimental Section

Preparation of Compounds. Maleonitriledithiolate, Disodium Salt (Na_2mnt).—This ligand was prepared by modification of procedures published by Bähr and Schleitzer¹⁶ and Locke and McCleverty.¹⁷ Sodium cyanide (81.7 g) was suspended in 500 ml of DMF and 126.6 g of CS_2 was added over 20 min with vigorous stirring and constant cooling. The cooling was removed and the stirring was continued for 1 hr. The resulting dark substance was taken up in 2000 ml of $CHCl_3$ and filtered. The $CHCl_3$ solution was refluxed for 24 hr during which time a yellow precipitate formed. The solution was filtered hot to yield 65 g of Na_2mnt which was found suitable for use in the preparations described below.

$[(C_6H_5)_4As]_2[Ti(mnt)_3]$.—With nitrogen rapidly bubbling through the solution, 2.5 g of $[(C_6H_5)_4As]Cl$ was dissolved in 150 ml of absolute ethanol and the bubbling was continued for 0.5 hr. Na_2mnt (1.8 g) was then added to the solution followed by the addition of 0.7 g of $TiCl_3$ as a solid in ~ 0.05 -g portions over about 10 min. The solution turned dark brown and after a few minutes the presence of a green precipitate was apparent. The nitrogen bubbling was continued for 0.5 hr. The copious green precipitate now present was collected on a fritted funnel and washed with 100 ml of absolute ethanol. The green precipitate was taken up in CH_2Cl_2 to give a red-purple solution. After addition of absolute ethanol, the solution was evaporated on a rotary evaporator to give a green microcrystalline precipitate. The precipitate was collected, washed with 100 ml of ethanol, air dried for 0.5 hr, and vacuum dried overnight to give 2.7 g of $[(C_6H_5)_4As]_2[Ti(mnt)_3]$ ($\sim 70\%$ yield based on Na_2mnt).

$[(C_6H_5)_4As]_2[V(mnt)_3]$.—This compound was prepared in good yield by Davison's procedure.¹³

$[N(CH_3)_4]_2[V(mnt)_3]$.—The general preparative procedure of Davison¹⁸ was used. The final recrystallizations were from acetone-water, acetone-2-propanol, and acetone-water. The

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(8) These ligands are variously referred to as dithiolenes⁹ and dithienenes¹⁰ and the nomenclature situation has been discussed by McCleverty.⁹ We use the term dithiolate here since this is generally the form of the uncomplexed ligand. The nomenclature should not be taken to imply electronic structural assignment for the complexes.

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TABLE I
 ANALYTICAL RESULTS ON MALEONITRILEDITHIOLATE COMPLEXES^a

Complex	% C		% H		% S		% N	
	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
$[(C_6H_5)_4As]_2[Ti(mnt)_3]$	58.33	58.51	3.26	3.25	15.57	15.56	6.83	6.70
$[(C_6H_5)_4As]_2[V(mnt)_3]$	58.19	58.45	3.25	3.29	15.53	15.36	6.81	6.68
$[(CH_3)_4N]_2[V(mnt)_3]$	38.77	38.76	3.91	4.07	31.08	30.90	18.09	17.88
$[(C_6H_5)_4As]_2[Cr(mnt)_3]$	58.14	58.30	3.25	3.41	15.52	15.75	6.81	6.75
$[(C_6H_5)_4As]_2[Mn(mnt)_3]$	58.00	56.98	3.24	3.22	15.48	15.30	6.79	6.64
$[(C_6H_5)_4As]_2[Fe(mnt)_3]$	57.96	58.45	3.24	3.38	15.47	15.38	6.79	6.83
$[(C_6H_5)_4As]_2[Mo(mnt)_3]$	56.14	55.80	3.14	3.15	14.99	14.68	6.58	6.61
$[(C_6H_5)_4As]_2[W(mnt)_3]$	52.55	51.73	2.94	3.06	14.03	13.20	6.15	6.04
$[(C_6H_5)_4As]_2[Re(mnt)_3]$	52.46	52.69	2.93	3.03	14.00	13.84	6.14	5.89
$[(C_6H_5)_4As]_3[Co(mnt)_3]$	61.90	60.86	3.71	3.70	11.81	11.67	5.18	5.13
$[N(C_4H_9)_4]_2[Mo(mnt)_3]$	52.75	51.98	7.25	7.26	19.22	18.50	11.18	10.97
$[N(C_4H_9)_4]_2[W(mnt)_3]$	48.50	48.90	6.66	6.64	17.65	17.93	10.31	10.21
$[N(C_4H_9)_4]_2[MoO(mnt)_3]$	54.74	53.58	8.28	8.16	14.62	15.19	9.64	9.77

^a Analyses performed by Galbraith Laboratories.

single crystals used for the X-ray studies were grown from acetone-2-propanol by slow evaporation from a partially covered crystallizing dish.

$[N(C_2H_5)_4]_2[Cr(mnt)_3]$.—This complex was also prepared by a modification of the literature method.¹³

$[(C_6H_5)_4As]_2[Cr(mnt)_3]$.—Hydrous chromic chloride ($CrCl_3 \cdot 6H_2O$, 1.22 g) was dissolved in 20 ml of absolute ethanol and added to 2.9 g of Na_2mnt suspended in 50 ml of hot ethanol. The solution was stirred for 10 min while being allowed to cool and was then filtered into 4.3 g of $[(C_6H_5)_4As]Cl$ in 50 ml of ethanol. The resulting precipitate was collected and recrystallized twice from CH_2Cl_2 -ethanol by using the rotary evaporator. (The solution is brown and gives the characteristic red color of $Cr(mnt)_3^{3-}$ when BH_4^- is added.) The yield is 2.2 g (~55% based on Na_2mnt).

$[(C_6H_5)_4As]_3[Cr(mnt)_3]$.—This complex was prepared by Davison's procedure.¹³

$[(C_6H_5)_4As]_2[Mn(mnt)_3]$.— Na_2mnt (1.4 g) and $[(C_6H_5)_4As]Cl$ (2.9 g) were placed in 100 ml of absolute ethanol on a steam bath with nitrogen bubbling through the solution. $Mn(ac)_3 \cdot 2H_2O$ (0.9 g) (ac = acetate) was added slowly as a solid to the hot ethanol mixture. The heating was continued for 5 min during which time a green precipitate appeared. The solution was then placed on a magnetic stirrer and cooled with continued nitrogen bubbling. Filtration yielded a green precipitate that became somewhat brownish on the surface while being air dried. The complex was recrystallized twice from CH_2Cl_2 -2-propanol with the final recrystallization and filtration carried out under nitrogen. The yield is 0.9 g of complex. This method of preparation is similar to one due to Williams.¹⁸

$[(C_6H_5)_4As]_2[Fe(mnt)_3]$.— $FeCl_3 \cdot 6H_2O$ (0.9 g) was dissolved in 75 ml of ethanol and added to 1.4 g of Na_2mnt . The resulting green solution was stirred for 15 min and filtered into 3.0 g of $[(C_6H_5)_4As]Cl$ in 50 ml of absolute ethanol. The green powder deposited was collected and recrystallized from CH_2Cl_2 -ethanol to give 2.5 g (80% based on Na_2mnt).

$[(C_6H_5)_4As]_3[Co(mnt)_3]$.— $Na_2Co(CO_3)_3 \cdot 3H_2O$ ¹⁹ (0.7 g) was suspended in 75 ml of absolute ethanol and added to 1.5 g of Na_2mnt in 150 ml of absolute ethanol on a steam bath. Upon heating (boiling) for 2.5 hr, the solution turned a very dark brown-green and was filtered hot into 4.5 g of $[(C_6H_5)_4As]Cl$ in 100 ml of cold absolute ethanol. After standing for 0.5 hr, the solution was filtered to yield a brown precipitate. This precipitate was dissolved in acetone and filtered, and 2-propanol was added. The solution was then allowed to stand overnight and lustrous black crystals of $[(C_6H_5)_4As]_3[Co(mnt)_3]$ were deposited.

$[(C_6H_5)_4As]_2[Mo(mnt)_3]$.— Na_2mnt (1.6 g) was suspended in 150 ml of absolute ethanol, and 0.8 g of $MoCl_5$ in 30 ml of ethanol (light green solution) was added gradually with stirring. After

1 hr of stirring, this solution was filtered into 2.4 g of $[(C_6H_5)_4As]Cl$ in ethanol to give an immediate green precipitate. After standing for 10 min, the solid was collected, recrystallized from CH_2Cl_2 -ethanol, and washed extensively with ethanol yielding 2.4 g (~50% based on Na_2mnt) after air and vacuum drying.

$[N(C_4H_9)_4]_2[Mo(mnt)_3]$.— Na_2mnt (2.79 g) was suspended in 20 ml of ethanol and 1.4 g of $MoCl_5$ in 10 ml of ethanol was added. After allowing the mixture to stand for 0.5 hr, 1.6 g of $N(C_4H_9)_4Br$ was added and green crystals appeared after several minutes; after 30 min the crystals were collected, recrystallized from CH_2Cl_2 , and washed thoroughly with ethanol and ether.

$[N(C_4H_9)_4]_2[MoO(mnt)_3]$.—This compound was isolated as a side product in the preparation of the tetrabutylammonium salt of $Mo(mnt)_3^{2-}$. It separated from the original reaction solution after the tris complex had been removed and also after the solution had stood over the weekend in an unstoppered flask. The product is light green and the crystals have a metallic luster. The complex was recrystallized by the CH_2Cl_2 -ethanol procedure. The identification of this complex as the molybdenyl species was confirmed by the presence in the infrared spectrum of an intense band assignable to $\nu(Mo-O)$ at 930 cm^{-1} .

$[(C_6H_5)_4As]_2[W(mnt)_3]$.—This compound was made in 40% yield in a manner identical with that used for $[(C_6H_5)_4As]_2[Mo(mnt)_3]$.

$[N(C_4H_9)_4]_2[W(mnt)_3]$.—Crude WCl_6 (0.97 g) was dissolved in 10 ml of ethanol and added to a solution of 1.4 g of Na_2mnt in 20 ml of ethanol. The resulting purple solution was allowed to stand for 10 min and 1.6 g of tetrabutylammonium bromide was added. The solution was then cooled in an ice-HCl bath and the resulting crystals were collected, recrystallized from CH_2Cl_2 -ethanol, washed with ether, and vacuum dried overnight.

$[(C_6H_5)_4As]_2[Re(mnt)_3]$.—The preparation of a pure sample of this compound proved difficult and it was found necessary to carry out all operations under nitrogen. Na_2mnt (1.7 g) was suspended in absolute ethanol with nitrogen bubbling. $[(C_6H_5)_4As]Cl$ (2.1 g) was added to the solution followed by $ReCl_5$ (0.91 g) and the solution was stirred with continued N_2 bubbling for 15 min during which time a deep green color appeared. Filtration (under nitrogen) yielded a green solid which under a microscope revealed itself as a mixture of green and yellow crystals. The solid was taken up in acetone, ethanol was added, and the acetone was removed by rotary evaporation. The ethanol, now yellow, contained a dark precipitate. The solution was filtered hot and then washed with cool ethanol and ether. The above recrystallization procedure was repeated three times to yield a pure sample of $[(C_6H_5)_4As]_2[Re(mnt)_3]$.

Physical Measurements.—X-Ray powder diffraction patterns were measured using a Norelco powder diffractometer. Conductances were determined at room temperature (23–26°) on an Industrial Instruments bridge, Model RC 16B2, using a cell calibrated with 0.01 M KCl solution. Electronic spectra were measured by means of a Cary Model 14 recording spectrophotometer. Spectral grade solvents were used throughout.

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Solid spectra were obtained with the same instrument by using Nujol mulls supported on filter paper. Infrared spectra were obtained with a Perkin-Elmer Model 441 or Model 137 spectrophotometer using the KBr-wafer and Nujol-mull techniques. Static susceptibility measurements were made at room temperature by the Gouy method, using $\text{Hg}[\text{Co}(\text{SCN})_4]$ as a calibrant. Polarographic measurements were made in acetonitrile solution with a dropping mercury or a rotating platinum electrode using an electronic polarograph. Triangular wave chronoamperometry (oscillopolarography) was utilized, with a platinum electrode serving as indicator electrode. Silver-silver perchlorate was used as a reference electrode [$\text{Ag}|\text{AgClO}_4 (0.1 M)|[(n\text{-C}_6\text{H}_7)_4\text{N}]\text{-ClO}_4 (0.1 M)$]. Solutions were approximately 0.001 *M* in complex and 0.1 *M* in tetra-*n*-propylammonium perchlorate. Electron spin resonance spectra were recorded at room temperature using a Varian V4502 spectrometer employing 100-kc/sec field modulation. The klystron frequency was measured directly from a wave meter, and the field was measured from a previously calibrated field dial. Low-temperature spectra were measured at 77°K using a Varian V4546 liquid nitrogen accessory.

Results

Synthetic Results.—The syntheses of the tris complexes were in general quite straightforward, but the minor variations necessary for the various metals proved somewhat problematical. These are, therefore, reported in the Experimental Section while some general considerations are presented below. All of the complexes gave highly satisfactory analytical results, and these are summarized in Table I. In Table II, some selected physical properties are presented for the complexes prepared in this study.

In the preparation of the dianionic complexes, the starting material was the appropriate metal chloride except for the Mn compound, where the tris-acetato complex was used. The general procedure is to allow the chloride and Na_2mnt to react in ethanol and then filter the solution containing the complex anion, presumably now present as the ethanol-soluble sodium salt. This filtrate is then added to excess $[(\text{C}_6\text{H}_5)_4\text{As}]\text{-Cl}$ in ethanol leading to the precipitation of $[(\text{C}_6\text{H}_5)_4\text{As}]_2\text{-}[\text{M}(\text{mnt})_3]$ with NaCl, excess Na_2mnt , and other side products remaining in solution to a large extent. The solid is then taken up in CH_2Cl_2 and filtered to leave behind NaCl and other impurities, and final crystallization is effected by addition of ethanol and slow removal of CH_2Cl_2 by means of a rotary evaporator at room temperature.

For the Mn and Ti complexes, a variant of the above procedure was found to be necessary. The Na_2mnt and $[(\text{C}_6\text{H}_5)_4\text{As}]\text{-Cl}$ were first placed in absolute ethanol with nitrogen bubbling through the solution. The precise amount of metal salt (TiCl_3 or $\text{Mn}(\text{ac})_3 \cdot 2\text{H}_2\text{O}$) was then added slowly to this solution as a solid. Thus, the $(\text{C}_6\text{H}_5)_4\text{As}^+$ salts were precipitated immediately upon formation of the dianions, this being necessary because of the relative solution instability of the complexes. The Ti complex was recrystallized from CH_2Cl_2 -ethanol, and it is interesting to note that the intense red-purple solution deposits sparkling green crystals. Recrystallization of the Mn complex must be done under nitrogen, if a pure sample is to be obtained. It is not advisable to leave either the Ti or the Mn complex in solution for an extended period of time

TABLE II
PHYSICAL PROPERTIES OF TRIS-MNT COMPLEXES

Complex	Mp, °C ^a	Color	Conductivity ^b
$[(\text{C}_6\text{H}_5)_4\text{As}]_2[\text{Ti}(\text{mnt})_3]$	213–215	Green (red-purple) ^c	127
$[(\text{CH}_3)_4\text{N}]_2[\text{V}(\text{mnt})_3]$	230–232	Green ^d	151
$[(\text{C}_2\text{H}_5)_4\text{N}]_2[\text{V}(\text{mnt})_3]$	155–157	Green ^d	141
$[(\text{C}_6\text{H}_5)_4\text{As}]_2[\text{Cr}(\text{mnt})_3]$	210–214	Brown	136
$[(\text{C}_6\text{H}_5)_4\text{As}]_2[\text{Mn}(\text{mnt})_3]$	176–181	Green	142
$[(\text{C}_6\text{H}_5)_4\text{As}]_2[\text{Fe}(\text{mnt})_3]$	196–200	Green	137
$[(\text{C}_6\text{H}_5)_4\text{As}]_2[\text{Mo}(\text{mnt})_3]$	267–270	Green	137
$[\text{N}(\text{C}_4\text{H}_9)_4]_2[\text{Mo}(\text{mnt})_3]$	177–178	Green	136
$[(\text{C}_6\text{H}_5)_4\text{As}]_2[\text{W}(\text{mnt})_3]$	263–265	Red-purple	138
$[\text{N}(\text{C}_4\text{H}_9)_4]_2[\text{W}(\text{mnt})_3]$	179–180	Red-purple	136
$[(\text{C}_6\text{H}_5)_4\text{As}]_2[\text{Re}(\text{mnt})_3]$	260–265	Green	134
$[(\text{C}_6\text{H}_5)_4\text{As}]_3[\text{Co}(\text{mnt})_3]$	173–174	Green-brown	208
$[\text{N}(\text{C}_4\text{H}_9)_4]_2[\text{MoO}(\text{mnt})_2]$	138–139	Green	120

^a Uncorrected. ^b In $\text{cm}^2 \text{mol}^{-1}$ in $10^{-3} M$ nitromethane solution. ^c Compound is green in solid but red-purple in solution. The red-purple solution decomposes to give a light yellow solution. ^d The color of this compound is quite unusual as it appears green in fluorescent light or outdoors on a cloudy day but appears red-brown in incandescent light. This is due to the presence in the visible region of two areas of maximum transmittance (one at 13,330 and one at 20,200 cm^{-1}).

because each decomposes to give a yellow solution. The $[(\text{C}_6\text{H}_5)_4\text{As}]_3[\text{Re}(\text{mnt})_3]$ complex was quite difficult to prepare (with $\text{ReO}(\text{mnt})_2^{2-}$ being a possible impurity), and the detailed steps required to produce a pure compound are given in the Experimental Section.

Of the trianionic complexes, $[(\text{C}_6\text{H}_5)_4\text{As}]_3[\text{Cr}(\text{mnt})_3]$ was made by a standard procedure,¹³ while the corresponding salt of $\text{Co}(\text{mnt})_3^{3-}$ was made from the tris-(carbonato)cobaltate in a manner analogous to the preparation of the $(n\text{-C}_6\text{H}_7)_4\text{N}^+$ salt.²⁰

X-Ray Powder Results.—The X-ray powder patterns for all of the known $[(\text{C}_6\text{H}_5)_4\text{As}]^+$ salts of tris-mnt complexes are presented in Table III. Inspection reveals that the complexes fall into at least three distinct groups. The first group consists of the two trianionic complexes which show extremely similar patterns. As expected, they are quite different from the dianionic complexes, and we conclude that $[(\text{C}_6\text{H}_5)_4\text{As}]_3[\text{Cr}(\text{mnt})_3]$ and $[(\text{C}_6\text{H}_5)_4\text{As}]_3[\text{Co}(\text{mnt})_3]$ are isomorphous and probably isostructural. A second group consists of the dianionic manganese and iron complex salts which show almost identical patterns and are thus considered isomorphous. The third group includes the dianionic complexes of Ti, V, Cr, Mo, W, and Re, whose powder patterns all closely resemble one another. The Ti, V, and Cr patterns are most similar, and we thus conclude that they are isomorphous. The Mo, W, and Re patterns appear to be sufficiently similar to each other and to those of Ti, V, and Cr that we tentatively conclude the six complexes form an isomorphous set. The small differences in *d* spacings may then be due to small differences in unit cell dimensions. The differences in intensities may be due to grinding and packing effects combined with the increase in metal scattering power in going from first- to second- and third-row metals. Another possibility which must, however, be

TABLE III
X-RAY POWDER DIFFRACTION RESULTS FOR
TRIS-mnt COMPLEXES

Complex	Interplanar (<i>d</i>) spacings of the most prominent peaks, Å
$[(C_6H_5)_4As]_2[Ti(mnt)_3]$	10.15 m, 9.10 w, 8.34 s, 7.75 vs, 7.38 s, 7.13 s, 6.75 s, 6.24 s, 5.90 s, 5.69 m, 5.47 vs, 5.12 w, 4.86 w, 4.47 w, 4.25 s, 4.12 vs, 3.92 w, 3.78 m, 3.72 m, 3.64 w, 3.49 w, 3.37 w, 3.32 m, 3.24 m
$[(C_6H_5)_4As]_2[V(mnt)_3]$	10.15 m, 9.10 m, 8.33 s, 7.76 vs, 7.37 s, 7.13 s, 6.76 s, 6.20 s, 5.87 s, 5.68 s, 5.46 vs, 5.18 m, 4.83 w, 4.44 w, 4.21 m, 4.07 s, 4.03 w, 3.89 w, 3.80 w, 3.67 m, 3.48 m, 3.40 w, 3.35 w, 3.33 m, 3.24 w
$[(C_6H_5)_4As]_2[Cr(mnt)_3]$	10.15 m, 9.02 w, 8.27 s, 7.75 vs, 7.24 s, 7.20 s, 6.75 s, 6.20 s, 5.85 s, 5.74 m, 5.40 vs, 4.87 w, 4.23 m, 4.13 vs, 3.91 m, 3.83 w, 3.74 m, 3.71 m, 3.63 m, 3.44 w, 3.36 w, 3.32 w, 3.30 w, 3.22 w
$[(C_6H_5)_4As]_2[Mn(mnt)_3]$	11.20 w, 7.62 vs, 6.75 w, 6.15 m, 5.99 m, 5.68 w, 5.40 m, 5.14 m, 5.05 w, 4.90 m, 4.48 w, 4.39 m, 4.13 w, 4.05 w, 3.80 w, 3.58 w, 3.50 w
$[(C_6H_5)_4As]_2[Mo(mnt)_3]$	10.04 vs, 9.40 m, 8.50 s, 7.70 vs, 7.44 m, 7.07 m, 6.85 m, 6.70 w, 6.15 s, 5.86 vs, 5.58 vs, 5.45 m, 5.15 w, 4.80 w, 4.43 w, 4.35 w, 4.23 w, 4.05 vs, 3.92 w, 3.82 m, 3.70 s, 3.58 w, 3.48 w, 3.42 w, 3.31 w
$[(C_6H_5)_4As]_2[W(mnt)_3]$	9.97 vs, 9.21 m, 8.43 m, 7.55 vs, 7.30 m, 7.02 m, 6.81 s, 6.10 s, 5.80 vs, 5.50 vs, 5.10 w, 5.00 w, 4.75 w, 4.41 m, 4.32 w, 4.03 vs, 3.89 w, 3.80 m, 3.68 s, 3.56 w, 3.45 w, 3.40 w, 3.32 w
$[(C_6H_5)_4As]_2[Re(mnt)_3]$	10.29 vs, 9.20 m, 8.34 w, 7.75 s, 7.37 s, 7.13 s, 6.82 s, 6.32 s, 5.90 vs, 5.45 vs, 5.15 w, 4.84 w, 4.44 w, 4.15 w, 4.12 vs, 3.92 w, 3.85 w, 3.80 m, 3.72 m, 3.62 w, 3.49 w, 3.37 w
$[(C_6H_5)_4As]_3[Cr(mnt)_3]$	16.40 w, 13.20 w, 11.62 w, 10.80 w, 10.30 w, 9.03 m, 8.75 w, 8.10 w, 7.76 m, 7.37 vs, 7.07 s, 6.97 w, 6.61 w, 6.14 w, 6.06 w, 5.83 w, 5.68 m, 5.36 s, 5.17 vs, 5.04 w, 4.87 w, 4.83 m, 4.64 s, 4.50 m, 4.35 m, 4.20 w, 4.12 w, 4.04 s, 4.00 w, 3.88 m, 3.73 w, 3.49 w, 3.39 m, 3.33 w
$[(C_6H_5)_4As]_2[Co(mnt)_3]$	16.40 w, 13.20 w, 11.62 w, 10.91 w, 10.40 m, 9.02 m, 8.75 m, 8.20 s, 7.70 m, 7.37 vs, 7.13 s, 6.55 w, 6.20 w, 6.10 w, 5.99 w, 5.82 w, 5.64 m, 5.40 s, 5.18 vs, 4.90 w, 4.82 m, 4.66 s, 4.47 s, 4.33 m, 4.19 m, 4.04 vs, 3.91 m, 3.87 w, 3.73 m, 3.64 w, 3.56 w, 3.40 m, 3.32 w

considered is that the compounds are indeed isomorphous (that is, they crystallize in the same space group with similar unit cell dimensions) but that the complex anions are in fact not isostructural. This could also account for the observed differences.

Electronic Spectral Results.—The electronic spectra

of the complexes are shown in Table IV. The spectra are not as intense as those of tris- $S_2C_2(C_6H_5)_2$ and tris-tdt complexes, which generally exist in the more highly oxidized monoanionic and neutral forms. A similar situation occurs in the bis planar complexes of these ligands^{21,22} where the dianionic forms are less highly colored.

Some similarities in the spectra can immediately be noted. Thus, all of the first-row complexes have a band close to $15,500\text{ cm}^{-1}$ of moderate extinction coefficient. Closer scrutiny reveals that complexes of metals which are adjacent to each other in the periodic table have at least one other band in common. All of the dianionic complexes are green, with the exception of the W complex which is red-purple. This is clearly reflected in the spectrum of the W complex; its first absorption maximum is at $17,500\text{ cm}^{-1}$, leaving the red region open for transmittance.

Magnetic Susceptibility and Electron Spin Resonance Results.—The magnetic susceptibility results are displayed in Table V and are for solid samples. Where there is overlap, our results are in reasonable agreement with recently published values of McCleverty and coworkers.¹⁵ It should be noted that the recorded values are all close to spin-only values which, in the absence of intermolecular cooperative effects, seem to be common for complexes of dithiolate ligands. It is, therefore, a simple matter to designate the number of unpaired spins in each of the complexes and this is also shown in Table V.

Our measurement of the solution esr spectrum of $V(mnt)_3^{2-}$ is in agreement with measurements by Davison, *et al.*,¹³ and by Atherton, *et al.*²³ The only other $S = 1/2$ system in this series is $Re(mnt)_3^{2-}$. This complex shows no esr signal at room temperature in the solid state (polycrystalline) nor in solution. This behavior is somewhat unusual for an $S = 1/2$ dithiolate complex and probably indicates an extremely short electron spin lattice relaxation time.

Polarographic Results.—The polarographic results are set out in Table VI. Some of Davison's results^{13,24} converted approximately to our scale²⁵ are also included, as are results for some related $S_2C_2(C_6H_5)_2$ complexes. We report here only complexes that show reversible waves. Thus, $Ti(mnt)_3^{2-}$ and $Mn(mnt)_3^{2-}$ decompose rapidly in the solvent-electrolyte medium, while $Fe(mnt)_3^{2-}$ and $Co(mnt)_3^{3-}$ give irreversible waves suggesting the possibility of partial dissociation to the corresponding stable bis-dithiolate complexes. The results clearly show that, as expected, the mnt complexes are much more easily reduced than any of the other tris-dithiolate complexes. For example, inspection of Table VI reveals a difference averaging

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(25) From a comparison of a number of couples run on both scales, a value of +0.4 V is estimated as bringing Davison's results^{13,24} to our scale.¹⁸

TABLE IV
SPECTRAL RESULTS FOR TRIS-mnt COMPLEXES

Complex	Band maxima, ^a cm ⁻¹ (ε in parentheses)
[(C ₆ H ₅) ₄ As] ₂ [Ti(mnt) ₃] ^b	15,620, 21,570, 26,320
[N(C ₆ H ₅) ₄] ₂ [V(mnt) ₃]	10,850 (2800), 15,040 (2000), 17,240 (4700), 19,050 (5000), 23,400 (6000), 26,500 (9000)
[(C ₆ H ₅) ₄ As] ₂ [Cr(mnt) ₃]	10,020 (190), 15,540 (2600), 17,240 (2200), 20,620 (4100), 27,400 (11,200)
[(C ₆ H ₅) ₄ As] ₃ [Cr(mnt) ₃]	14,920 (390), 17,890 (1400), 21,370 (5850), 23,640 (7810), 29,070 (11,800)
[(C ₆ H ₅) ₄ As] ₂ [Mn(mnt) ₃] ^c	12,000 (1900), 15,800 (2160), 17,200 (1800)
[(C ₆ H ₅) ₄ As] ₂ [Fe(mnt) ₃] ^c	12,380 (3300), 15,500 (1000), 23,520 (7200)
[(C ₆ H ₅) ₄ As] ₃ [Co(mnt) ₃]	15,030 (400), 21,700 (4000)
[(C ₄ H ₉) ₄ N] ₂ [Mo(mnt) ₃]	14,980 (5800), 20,100 (2700), 25,670 (9900), 29,200 (11,000)
[(C ₄ H ₉) ₄ N] ₂ [W(mnt) ₃]	17,540 (4200), 20,410 (6700), 23,520 (3400), 26,670 (7700), 27,970 (6640)
[(C ₆ H ₅) ₄ As] ₂ [Re(mnt) ₃]	10,640 (900), 14,790 (4200), 25,380 (16,000)

^a Below 30,000 cm⁻¹ in acetonitrile solution except where noted otherwise. ^b Nujol mull. ^c Chloroform solution.

1.4 V for the corresponding waves in mnt and S₂C₂-(C₆H₅)₂ complexes.

Discussion

The synthetic, analytical, and conductivity results have confirmed the existence of the class of compounds [(C₆H₅)₄As]₂[M(mnt)₃] for M = Ti, V, Cr, Mn, Fe, Mo, W, and Re. While the stoichiometry of the complexes is definitely confirmed, the intimate details of molecular and electronic structure are still uncertain.

We now try to draw structural inferences from the available experimental data. The X-ray powder patterns indicate that the Ti, V, Cr, Mo, W, and Re complexes most likely belong to the same space group with similar unit cell dimensions. The Ti, V, and Cr patterns are so similar that we take this as evidence of a similar geometric arrangement for the anion atoms. However, owing to the distorted nature of the vanadium anion, the large size of the (C₆H₅)₄As⁺ cation, and the small intensity differences that are present, it is possible that small geometric differences will be found. The Mo, W, and Re complexes also appear to be isomorphous to the Ti, V, and Cr complexes, but here the intensity differences are such that a nonisostructural anion may in fact be present. Thus, from the X-ray data we infer that the Ti, V, and Cr complexes have (more or less) severely distorted structures, while no conclusions can be reached about the Mo, W, and Re complexes. The Fe and Mn compounds are mutually isomorphous and display patterns grossly different from the other dianionic complexes. We conclude that the Mn compound has the normal octahedral structure found¹² for Fe(mnt)₃²⁻. At this point it is appropriate to compare our results with those of McCleverty, *et al.*¹⁵ In the series of complexes [(C₆H₅)₄P]₂[M(mnt)₃] they suggest that the M = V, Cr, Mo, W, and Fe complexes are isomorphous. This result is intriguing in view of the known difference in the V(mnt)₃²⁻ and Fe(mnt)₃²⁻ structures; it points out the dangers in designating isomorphous structures as necessarily due to isostructural anions.

The magnetic properties of the first-row complexes are very revealing. If the ligands are considered to be

TABLE V
MAGNETIC SUSCEPTIBILITY RESULTS FOR TRIS-mnt COMPLEXES

Complex	μ_{eff} , BM	S
[(C ₆ H ₅) ₄ As] ₂ [Ti(mnt) ₃]	Diam	0
[(C ₆ H ₅) ₄ As] ₂ [V(mnt) ₃] ^a	1.82	1/2
[(C ₆ H ₅) ₄ As] ₂ [Cr(mnt) ₃] ^a	2.89	1
[(C ₆ H ₅) ₄ As] ₂ [Mn(mnt) ₃]	3.85	3/2
[(C ₆ H ₅) ₄ As] ₂ [Fe(mnt) ₃]	3.00	1
[N(C ₄ H ₉) ₄] ₂ [Mo(mnt) ₃]	Diam	0
[N(C ₄ H ₉) ₄] ₂ [W(mnt) ₃]	Diam	0
[(C ₆ H ₅) ₄ As] ₂ [Re(mnt) ₃]	1.61	1/2
[(C ₆ H ₅) ₄ As] ₃ [Cr(mnt) ₃] ^a	3.90	3/2
[(C ₆ H ₅) ₄ As] ₃ [Co(mnt) ₃]	Diam	0

^a Data from ref 13.

TABLE VI
POLAROGRAPHIC RESULTS FOR TRIS-mnt COMPLEXES^a

Complex	$E_{1/2}$ (V) for					
	0 → -1	-1 → -2	-2 → -3	-3 → -4		
[(C ₆ H ₅) ₄ As] ₃ [Cr(mnt) ₃] ^b		0.36	-0.24			
[(C ₆ H ₅) ₄ As] ₂ [V(mnt) ₃] ^b		0.25	-0.89			
[N(C ₄ H ₉) ₄] ₂ [Mo(mnt) ₃]	0.71	0.30	-1.37	-2.06		
[N(C ₄ H ₉) ₄] ₂ [W(mnt) ₃]		0.23	-1.64	-2.19		
[(C ₆ H ₅) ₄ As] ₂ [Re(mnt) ₃]	0.95	-0.35	-1.08	-2.09		
Mo(S ₂ C ₂ (C ₆ H ₅) ₂) ₃ ^c	-0.49	-1.10	-2.92			
W(S ₂ C ₂ (C ₆ H ₅) ₂) ₃ ^c	-0.54	-1.14	<-2.9			
Re(S ₂ C ₂ (C ₆ H ₅) ₂) ₃ ^c	-0.34	-1.18	-2.59			

^a Solutions in acetonitrile were 10⁻³ M in complex and 0.1 M in [(n-C₄H₉)₄N]ClO₄. A rotating Pt indicator electrode and a Ag/AgClO₄ (0.1 M) reference electrode were used. ^b Data from ref 13. ^c Data from ref 6.

dianions, then the central metals are in the formal IV oxidation state, and inspection of Table V shows that the magnetic moments are typical of low-spin, first-row octahedral complexes. It is pertinent to note here that the most readily obtained trianionic complexes are Cr(mnt)₃³⁻ ($\mu_{\text{eff}} = 3.89$ BM) and Co(mnt)₃³⁻ (diamagnetic). These anions form isomorphous tetraphenylarsonium salts and we recall that Co(III), d⁶, and Cr(III), d³, are considered to be the best central ions for octahedral structures. Furthermore, Co(mnt)₃³⁻ possesses a spectrum similar to that²⁶ of Co(dto)₃³⁻, which is known²⁷ to be octahedral.

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The evidence for second- and third-row complexes is much less compelling and here we can only speculate, keeping in mind the lack of direct structural evidence. The magnetic susceptibility data show that $\text{Mo}(\text{mnt})_3^{2-}$ and $\text{W}(\text{mnt})_3^{2-}$ [formally $\text{M}(\text{IV})$] are diamagnetic, while $\text{Re}(\text{mnt})_3^{2-}$ has $\mu_{\text{eff}} = 1.61$ BM, indicating one unpaired electron. These results can be accommodated either in D_3 -type octahedral or trigonal-prismatic (D_{3h}) coordination.

For example, in D_3 symmetry, the diamagnetism would require that the a_1 orbital be lowest with the e orbitals of sufficiently higher energy to cause spin pairing.²⁸ The Re complex would then be expected to have a 2E (orbitally degenerate) ground state. In D_{3h} symmetry, the scheme that we derived previously⁶ predicts diamagnetism for the W and Mo complexes and an orbitally degenerate ${}^2E'$ ground state for $\text{Re}(\text{mnt})_3^{2-}$. Thus either geometry can accommodate the observed magnetic susceptibility and electron spin resonance behavior.

The electronic spectral properties of the Mo and Re complexes are also of interest as they both show intense bands at $\sim 15,000$ and $\sim 25,000$ cm^{-1} similar to their neutral counterparts with $\text{S}_2\text{C}_2(\text{C}_6\text{H}_5)_2$ and tdt ligands. Based on our molecular orbital scheme⁶ we

(28) For a helpful discussion of the situation for D_3 complexes see ref 24.

would predict the $15,000\text{-cm}^{-1}$ band to be present in dianionic trigonal-prismatic complexes, but we would not expect the $25,000\text{-cm}^{-1}$ band to be present. To complicate matters further, the first band in the $\text{W}(\text{mnt})_3^{2-}$ spectrum occurs at substantially higher energy than the first band in the Re or Mo complex. These results are puzzling and we shall not attempt an explanation until the structural picture is clarified.

Finally, we inspect the polarographic data for the second- and third-row complexes. The trends in the half-wave potentials appear very much like those for $\text{M}(\text{S}_2\text{C}_2(\text{C}_6\text{H}_5)_2)_3$ complexes (see Table VI). Thus the large jump in potential comes between the $(0 \rightarrow -1)$ and $(-1 \rightarrow -2)$ waves for the Re complexes, while it occurs between the $(-1 \rightarrow -2)$ and $(-2 \rightarrow -3)$ waves for the Mo and W complexes. These results indicate a qualitative similarity in electronic energy levels in the two sets of complexes and thus are not inconsistent with the possibility that the tris-mnt ones have trigonal-prismatic structures. Further structural work in this area is obviously needed.

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1,7-Phosphacarbollylnickel¹ Complexes Containing Allyl, Cyclopropenyl, or Nitrosyl Ligands

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The synthesis and characterization of 1,7-phosphacarbollylnickel complexes containing allyl, cyclopropenyl, or nitrosyl ligands are described. The asymmetry of the 1,7-phosphacarbollyl ligand is reflected in the unusual proton nmr spectra of the allyl and 2-methallyl complexes.

Stable cyclopentadienyl compounds of nickel occur in which the valence shell formally contains 18, 19, or 20 electrons. Nickelocene is a 20-electron system which can be readily oxidized to the formal Ni(III) ion, $(\pi\text{-C}_5\text{H}_5)_2\text{Ni}^+$. At lower temperature (-40°) further oxidation has been observed electrochemically to give

(1) The numbering system employed in this article follows the new nomenclature rules which recently appeared in *Inorg. Chem.*, **7**, 1945 (1968). Unfortunately, two numbering systems have been suggested for *closo* transition metal complexes. One method suggests that the *nido* borane ligand be numbered prior to (rule 2.321) incorporation into the metal complex [e.g., $(\text{C}_3\text{H}_5)\text{Ni}(\text{7,9-B}_9\text{H}_9\text{CHPC}_3\text{H}_3)$]. The other method numbers the *closo* complex considering the metal atom as part of the cage [e.g., $(\text{C}_3\text{H}_5)\text{Ni}(\text{1,7-B}_9\text{H}_9\text{CHPC}_3\text{H}_3)$]. The latter method avoids the difficulty of translating from one numbering system to another when comparing closely related icosahedral systems. It is hoped that the nomenclature committee will rapidly clarify this numbering system ambiguity.

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the 18-electron ion $(\pi\text{-C}_5\text{H}_5)_2\text{Ni}^{2+}$.⁸ A phosphacarborene analog of nickelocene, $(\text{1,7-B}_9\text{H}_9\text{CHPC}_3\text{H}_3)_2\text{Ni}$, has also been reported.⁴ The mixed sandwich molecule $(\text{C}_3\text{H}_5)\text{Ni}(\text{1,2-B}_9\text{C}_2\text{H}_{11})$ has been prepared and represents an example of a stable 19-electron system.³ Stable 18-electron bis(π -ligand)nickel(IV) molecules have been formed using the $\text{B}_{10}\text{H}_{10}\text{CH}^3-$ and 7,8- and 7,9- $\text{B}_9\text{C}_2\text{H}_{11}^{2-}$ ions.^{5,6} Although all of these ligands are

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