Studies on Nickel, Palladium, and Platinum Dithiolates

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The preparation, optical, and electrical conductivities of nickel, palladium, and platinum complexes of $S_2C_2R_2^{2-}$ ligands (where R = CN, Me, Ph, or H) are described together with attempts to produce new one-dimensional metals based on these metal complexes.

Over the past decade there has been much work on the preparation and properties of one-dimensional (1-D) metallic complexes.[1] Although most of this work has been concentrated on the partially oxidised tetracyanoplatinates and bis(oxalato)-platinates, a recent and significant development has been the discovery of the new 1-D metal complex $Li_{0.75}[Pt\{S_2C_2(CN)_2\}_2]\cdot 2H_2O$.[2,3] The preparation,[2] properties,[3] and crystal structure [4] of this compound have been reported and it is clear that the conduction pathway in this compound is different from those in previously studied 1-D metallic complexes since the crystal structure shows that the ligand orbitals must be involved. The effect of varying the cation on the properties of this type of compound has been discussed briefly elsewhere.[5]

This paper discusses the electrical conduction properties of integral oxidation state complexes of Ni, Pd, and Pt with dithiolate ligands $S_2C_2R_2^{2-}$ where R = CN, Et, Me, or H, and reports attempts to prepare 1-D metallic complexes which are analogues of $Li_{0.75}[Pt\{S_2C_2(CN)_2\}_2]\cdot 2H_2O$ containing other substituted dithiolate ligands.

Experimental

Preparation of Compounds.—The complexes $[M(S_2C_2Ph_2)_2]$ (where M = Ni, Pd, or Pt) were prepared by the method of Schrauzer and Mayweg.[6] The compounds $[NEt_4][M(S_2C_2Ph_2)_2]$ (M = Ni or Pt) were prepared by the method of Davison *et al.*[7] using reduction with *p*-phenylenediamine in dimethyl sulphoxide and also by the method of Schrauzer and Mayweg [8] involving reduction with potassium metal and subsequent addition of NEt_4Br in ethanol. The complexes $K[M(S_2C_2Ph_2)_2]$ (M = Ni, Pd, or Pt) were prepared by the method of Schrauzer and Mayweg[8] using dry benzene or xylene as solvents.

Attempts to prepare the Li^+ or NH_4^+ salts by reduction with either *p*-phenylenediamine or potassium metal followed by the addition of LiCl or NH_4Cl were unsuccessful and led either to products with a much higher than expected carbon content or to the potassium salt. Attempts were also made to prepare metallic complexes by using the same technique used for the production of $Li_{0.75}[Pt\{S_2C_2(CN)_2\}_2]\cdot 2H_2O$; [3] $[NEt_4][Ni(S_2C_2Ph_2)_2]$ was dissolved in a mixture of acetone in water and converted to the acid form using a cation exchange resin. Lithium chloride was added to the resulting solution. A black microcrystalline product was obtained but with a much higher carbon content than that expected for an analogue of $Li_{0.75}[Pt\{S_2C_2(CN)_2\}_2]\cdot 2H_2O$.

The complexes $[M(S_2C_2Me_2)_2]$ (M = Ni or Pt) were prepared by a similar method to that used for $[M(S_2C_2Ph_2)_2]$ but using acetoin in place of benzoin. The reduction of $[Ni(S_2C_2Me_2)_2]$ by potassium in benzene solution was studied, but the product oxidised on exposure to air to give the neutral starting material and therefore the product was not studied further.

Disodium ethylene-1,2-dithiolate was prepared from the commercially available *cis*-1,2-dichloroethene and α-toluenethiol by the method of King and Eggers.[9] Complexes of $[M(S_2C_2H_2)_2]$ (M = Ni or Pt) were prepared by the method of Hoyer and Schroth.[10]

Attempts to oxidise $[M(S_2C_2Ph_2)_2]$ or $[M(S_2C_2Me_2)_2]$ (M = Ni or Pt) with iodine or bromine in dichlorobenzene or dichloromethane were unsuccessful. With iodine no reaction occurred whilst the complex decomposed on reaction with bromine. The decomposition product has been shown to be tetraphenyl-1,4-dithiin.[11]

Attempts to oxidise or reduce $[M(S_2C_2Ph_2)_2]$ or $[M(S_2C_2Me_2)_2]$ in solution using electrolytic methods at voltages up to 2 V also failed to yield any metallic complexes. Analyses of the complexes studied are given in Table 1.

Physical Measurements.—*Electrical conductivity.* The electrical conductivity measurements were made on compressed pellets. Samples were ground by hand in an agate pestle and mortar, degassed, and compacted at 9 ton in^{-2} pressure (*ca.* 1.4×10^8 Pa) for 3—5 min. Aquadag (colloidal graphite) was used as the contact material between the pellet and gold wire leads. The conductivity was measured at a constant d.c. voltage of between 1 and 10 V supplied by a Hewlett Packard 740-A standard/differential voltmeter. The current was measured with a Keighley 602 solid-state electrometer. All samples gave ohmic behaviour under the conditions of measurement.

Table 1. Analyses of compounds

	Found (%)				Calc. (%)			
Compound	C	H	N	M	C	H	N	M
$[Ni(S_2C_2Ph_2)_2]$	62.2	3.65		10.7	61.9	3.7		10.8
$[Pd(S_2C_2Ph_2)_2]$	56.8	3.55		18.3	56.9	3.4		18.0
$[Pt(S_2C_2Ph_2)_2]$	49.6	3.2			49.4	2.9		
$[NEt_4][Ni(S_2C_2Ph_2)_2]$	64.05	5.75	1.85	9.3	64.2	6.0	2.10	8.7
$[NEt_4][Pt(S_2C_2Ph_2)_2]$	51.25	4.65	1.75		53.4	4.9	1.7	
$K[Ni(S_2C_2Ph_2)_2]$	56.35	3.5		9.55	57.8	3.5		10.1
$[Ni(S_2C_2Me_2)_2]$	32.7	3.95		19.4	32.55	4.05		19.9
$[Pt(S_2C_2Me_2)_2]$	22.75	2.75			22.25	2.8		

Table 2. Electrical conductivity and absorption spectra

Compound	σ/Ω^{-1} cm^{-1} (compressed pellet)	$\lambda_{max.}$/cm^{-1} ($\pi\rightarrow\pi^*$)
$[Ni(S_2C_2Ph_2)_2]$	5×10^{-11}; 2×10^{-9} [a]	11 490
$[Pd(S_2C_2Ph_2)_2]$	2×10^{-11}	11 760
$[Pt(S_2C_2Ph_2)_2]$	1×10^{-12}; 2.5×10^{-11} [a]	11 760
$[NEt_4][Ni(S_2C_2Ph_2)_2]$	1×10^{-6}	10 640, 11 100
$[NEt_4][Pt(S_2C_2Ph_2)_2]$	$\sim10^{-6}$	10 100
$K[Ni(S_2C_2Ph_2)_2]$	1×10^{-7}	10 640
$K[Pt(S_2C_2Ph_2)_2]$	$\sim10^{-6}$	
$[Ni(S_2C_2Me_2)_2]$	1×10^{-9}; 1.6×10^{-9} [a]	10 750
$[Pt(S_2C_2Me_2)_2]$	1.5×10^{-10}; 1.1×10^{-10} [a]	11 430
$[Ni(S_2C_2H_2)_2]$	2.2×10^{-6}; [b] $\sim10^{-7}$ [a]	11 760
$[NEt_4]_2[Ni\{S_2C_2(CN)_2\}_2]$	$<10^{-12}$; 2×10^{-12} [c]	
$[NEt_4][Ni\{S_2C_2(CN)_2\}_2]$	$\sim10^{-9}$; 3.4×10^{-5}; [b] 5×10^{-9} [c]	
$[NEt_4]_2[Pt\{S_2C_2(CN)_2\}_2]$	$\sim10^{-10}$	
$[NEt_4][Pt\{S_2C_2(CN)_2\}_2]$	$\sim10^{-8}$	

[a] Ref. 12. [b] Single-crystal measurement. [c] Ref. 17.

Reflectance spectra. Reflectance spectra were recorded on powdered samples using a Beckman DK-2A ratio recording spectrophotometer fitted with a standard reflectance attachment.

Infrared spectra. Spectra were recorded on a Perkin-Elmer 225 grating i.r. spectrophotometer between 4 000 and 200 cm^{-1} as mulls in Nujol or fluorocarbon oil between CsI plates.

Results and Discussion

The nature of the bonding in metal dithiolates has received a great deal of attention. From a study of the i.r. spectra of the neutral, monoanion, and dianion species the reduction is formulated as shown below.[12,13] The bonding in the neutral $[Ni(S_2C_2H_2)_2]$ molecule has been discussed by Schrauzer and Rabinowitz.[11,13] The most important molecular orbitals (m.o.) are the highest occupied m.o. (h.o.m.o.) and the lowest unoccupied m.o. (l.u.m.o.). The h.o.m.o. has $2b_{1u}$ symmetry and is formed by the combination of a B_{1u} ligand π m.o. with the metal $4p_z$ orbital. The l.u.m.o. ($3b_{2g}$ symmetry) is formed by the overlap of a B_{2g} ligand π m.o. with the $3d_{xz}$ orbital of the metal. Calculations indicate that the l.u.m.o. has 50—85% ligand character depending on the nature of the substituents on the ligand.[14] In the neutral complex the h.o.m.o. is full and the l.u.m.o. empty. Successive reductions to the mono- and di-anion place one and then two electrons in the l.u.m.o. of the neutral complex.

Reflectivity Studies.—All the complexes possess a very intense absorption band around 10 000—12 000 cm^{-1} as shown in Table 2. The position of the peak for the neutral complexes is very similar to that previously reported in solution.[15] This indicates that there are no interactions between the molecules in the solid state additional to those present in solution. This peak corresponds to the $2b_{1u} \longrightarrow 3b_{2g}$ transition and is found at slightly lower energies for the nickel complex compared with the platinum complex. In the monoanion the same transition is observed but at lower frequencies. This transition is absent in the dianion because the $3b_{2g}$ orbital is full and the lowest absorption band therefore occurs at much higher energies.

Polarographic studies have shown that the ease of reduction in solution follows the sequence of substituents CN > Ph > Me.[6,7] The reflectance spectra, however, show a different order for the energy of the $2b_{1u} \longrightarrow 3b_{2g}$ transition suggesting that polarographic studies carried out in solution may not necessarily be a good guide for predicting solid-state properties.

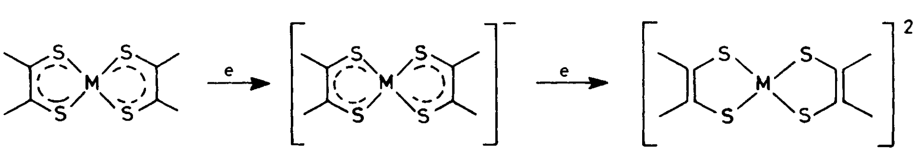
Electrical Conductivity Studies.—The values for the specific conductivities of the neutral complexes are in reasonable agreement with those reported by Rosa and Schrauzer.[16] However, whereas they reported that the specific conductivity for salts of the monoanions $[M(S_2C_2Ph_2)_2]^-$ were of the order of 10^{-13} Ω^{-1} cm^{-1} we find them to be 10^{-6}—10^{-7} Ω^{-1} cm^{-1}, and much higher than those of the parent neutral complex. Indeed all the results show that the monoanion complexes are considerably more conducting than either the corresponding neutral complex or the dianion. Rosseinsky and Malpas[17] have previously shown that $[Ni\{S_2C_2(CN)_2\}_2]^-$ salts are more conducting than $[Ni\{S_2C_2(CN)_2\}_2]^{2-}$ salts.

The mechanism for conduction in these materials must involve an activated hopping process similar to that found in organic crystals. The carrier electrons will be accommodated in the lowest available m.o. of the molecule. In the neutral complexes it has been suggested that generation and transmission must involve the formation of a monocation and a monoanion.[17]

$—M—M—M—M—M$ $—M—M^{+}—M^{-}—M—M$	carrier generation
$—M^{+}\ M—M—M^{-}—M$	carrier transmission
$—M^{-}—M^{-}—M^{-}—M^{-}—$ $—M^{-}—M—M^{2-}—M^{-}—$	carrier generation
$—M—M^{-}—M^{-}—M^{2-}—$	carrier transmission

On the other hand, in the case of the monoanion a neutral molecule and di-anion are produced. It is well established that whereas the neutral molecules of this series are easily reduced it is very difficult to oxidise them to stable cations. Thus the cationic carrier formation step outlined for the neutral molecule involving the formation of a cation would be expected to have a much higher activation energy than that of carrier formation in the monoanion. In the case of the nickel dithiolates this has been shown to correlate with the $\Delta E_{\frac{1}{2}}$ for the appropriate disproportionation reactions.[17] This therefore explains the differences observed between the neutral molecules and the monoanions.

It is clear from Table 2 that the monoanions containing the phenyl-substituted dithiolate ligand are at least 10^3 times more conducting than those of the cyano-substituted ligand. It might be thought that this too was a reflection of the relative ease of the disproportionation reactions of the corresponding complexes. Inspection of the relevant $\Delta E_{\frac{1}{2}}$ shows that this is not the case as the disproportionation reaction would appear



to be more favourable in the case of the cyano-substituted complexes.[7] Thus the difference in conductivity observed between the phenyl- and cyano-substituted monoanion complexes is probably associated with increased mobility of the charge carriers in the phenyl-substituted complexes.

The discovery that new 1-D metals could be synthesised based on $[M\{S_2C_2(CN)_2\}_2]$ (M = Pt or Ni) anions prompted the present study. As described in the Experimental section many attempts have been made to prepare similar highly conducting compounds based on $[M(S_2C_2Me_2)_2]$, $[M(S_2C_2Ph_2)_2]$, and $[M(S_2C_2H_2)_2]$ anions. Unfortunately none of these attempts was successful. It has been shown that the distribution of electron density in the monoanion $3b_{1g}$ orbital varies with the substituent on the ligand. Electron-withdrawing groups such as CN increase the electron density on the metal and reduce it on the S compared with phenyl substituents. This may aid the intermolecular overlap necessary for the formation of a 1-D metal.

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