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Charge Transfer Interactions between Transition Metal Compounds and Organic Acceptors

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Electron donor-acceptor interactions between inorganic complexes and organic donors and acceptors have been studied by visible absorption spectroscopy and electron spin resonance techniques. Attention has been concentrated on interactions between transition metal dithiolene complexes (D) and quinone acceptors (A). In many cases complete transfer of charge to give D^+ and A^- occurs in solution.

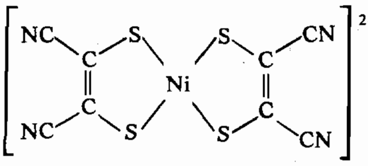
Introduction

There has recently been considerable interest in interactions between transition metal complexes and strong organic acceptors such as tetracyanoethylene or benzoquinones. This interest covers the preparation and properties of these complexes,[1] and their role as intermediates in substitution reactions[2] and in homogeneous catalysis.[3] We have studied electron donor-acceptor interactions between metal complexes, particularly dithiolenes, and organic acceptors and donors.

Interaction between a donor complex, D, and an acceptor, A, may give a simple molecular complex D.A., or may as a result of complete transfer of charge give the two ions D^+ and A^-. The molecular complex D.A. is normally, if somewhat proleptically, termed a « charge transfer complex ». This title refers to the characteristic spectrum in the visible-ultraviolet region of the spectrum arising from transitions from a largely non-bonding ground state with some admixture of the excited state $D^+ . A^-$ to a largely ionic excited state with some D . A character. The formation of D^+ and A^- rather than an essentially D . A ground state depends on ionisation potentials and electron affinities, and on solvation effects. The separate ions will obviously be favoured in a strongly solvating (high Z or E_T value[4]) solvent. These phenomena have been widely observed in organic systems, but only rarely reported for inorganic systems. Examples of the formation of D . A molecular complexes from metal complexes include the reaction of metal-oxine complexes with acceptors such as tetracyanoethylene and *p*-chloroanil,[5] while interaction between tetrahalogenometallate (MX_4^{n-}) anions and paraquat lead to D^+ plus A^- for $MX_4^{n-} \equiv FeCl_4^{n-}$, but to D . A for most of the other MX_4^{n-} studied.[6] In the present paper we report evidence from visible absorption and e.s.r. spectroscopy for interactions of the type $D + A \rightarrow D^+ + A^-$ between a variety of dithiolene complexes of transition metal ions and organic acceptors, especially 2,3-dichloro-5,6-dicyano-*p*-benzoquinone, and for a selection of other inorganic complex - organic acceptor or donor systems.

Results and Discussion

Wavelengths of maximum absorption of new bands which appear in the 500-700 mμ region on mixing dichloromethane solutions of dithiolene complexes, *e.g.* bis-maleonitriledithiolatonickel(II), $Ni(mnt)_2^{2-}$, formula I: *



I

and of 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (hereafter abbreviated to Q) are reported in Table I. The constancy of values in this Table, independent of the nature of the transition metal, the nature of the ligand, the charge on the complex, and the gegenion present, suggest that a common species, presumably Q^-, is generated in all cases. Table II suggests similar behaviour for the acceptors 7,7,8,8-tetracyanoquinodimethane (TCNQ) and tetracyanoethylene (TCNE). The observed spectra are thus internal transitions of A^- rather than charge-transfer $D . A \rightarrow D^+ . A^-$, since the latter would vary with D. Confirmation that the observed spectra do arise from $A^- \rightarrow A^{-*}$ transitions comes from comparison (Table III) with known A^- spectra generated by established donors such as N,

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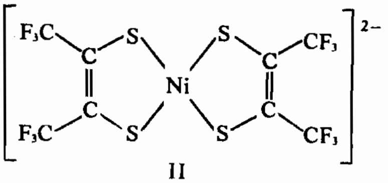
(1) E.g. W. H. Baddley, *Inorg. Chim. Acta Rev.*, *2*, 7 (1968).
(2) E.g. P. Uguagliati and W. H. Baddley, *J. Amer. Chem. Soc.*, *90*, 5446 (1968).
(3) E.g. G. Lugli, W. Marconi, A. Mazzel, and N. Palladino, *Inorg. Chim. Acta*, *3*, 151 (1969).
(4) C. Reichardt, *Angew. Chem. Internat. Ed.*, *4*, 29 (1965).
(5) A. S. Bailey, R. J. P. Williams, and J. D. Wright, *J. Chem. Soc.*, 2579 (1965).

(*) Actual oxidation states of transition metals in maleonitriledithiolato complexes are of course difficult to define, since there is much electron delocalisation between metal ion and ligands. In this paper we use the convention that each mnt ligand bears a 2- charge.
(6) A. J. Macfarlane and R. J. P. Williams, *J. Chem. Soc.* (*A*), 1517 (1969).

Table I. New bands observed in the region 500-700 mμ on mixing dichloromethane solutions of 2,3-dichloro-*p*-benzoquinone and maleonitriledithiolato, $M(mnt)_2^{n-}$, or 1,2-diperfluoromethylethylenedithiolato, $M(scf)_2^{n-}$, complexes.

(i) Metal variation (M^{II})	$(Et_4N)_2[Co(mnt)_2]$	544	584
	$(Et_4N)_2[Ni(mnt)_2]$	544	585
	$(Et_4N)_2[Cu(mnt)_2]$	542	584
	$(Et_4N)_2[Zn(mnt)_2]$	544	585
	$(Et_4N)_2[Pd(mnt)_2]$	542	583
	$(Et_4N)_2[Pt(mnt)_2]$	540	584
(ii) Metal variation (M^{III})	$(Et_4N)[Ni(mnt)_2]$	no new bands	
	$(Et_4N)[Pd(mnt)_2]$	(540)	(588)
	$(Et_4N)[Pt(mnt)_2]$	542	584
(iii) Ligand variation	$(Et_4N)_2[Ni(scf)_2]$	544	586
(iv) Gegenion variation	$(nBu_4N)_2[Ni(mnt)_2]$	544	585

N, N′, N′-tetramethyl-*p*-phenylenediamine (TMPD) or iodide. Table III also illustrates the effect of ionisation (redox) potential variation in donors. Bis-maleonitriledithiolatonickel(II), $Ni(mnt)_2^{2-}$, formula I above, is a fairly reluctant donor, giving anions only with the strongest acceptors TCNQ, TCNE, and Q, but the bis-(1,2-diperfluoromethylethylenedithiolato)nickel(II) complex, $Ni(scf)_2^{2-}$, formula II below, with its more favourable redox potential,[7] also generates A^- from the two dichloro-*p*-benzoquinones. Neither complex is a sufficiently powerful donor to generate A^- from *p*-benzoquinone or toluquinone.



II

Bis-maleonitriledithiolatonickel(III), $Ni(mnt)_2^-$, gives no A^- with Q; the corresponding palladium(III) and platinum(III) complexes do give some A^- from Q, though in the former case with considerable reluctance. These observations are consistent with the expected stabilities of the respective metal(IV) complexes which would be produced as D^+.

The generation of the respective anions from Q, from TCNE, and from *p*-chloroanil by the addition of a variety of dithiolene complexes, in dichloromethane solution, was confirmed by observation of a strong e.s.r. signal at the appropriate *g* value. E.s.r. spectroscopy should also give some information about the nature of the D^+ species generated from the dithiolene complex in the cases where D^+ is paramagnetic, and indeed a spectrum appropriate to $Ni(mnt)_2^-$ was observed from mixed dichloromethane solutions of $Ni(mnt)_2^{2-}$ and Q. The e.s.r. results from these and related experiments will be reported fully elsewhere.[8]

Table II. New bands observed on mixing dichloromethane solutions of 7,7,8,8-tetracyanoquinodimethane (TCNQ) or tetracyanoethylene (TCNE) with maleonitriledithiolato complexes, $M(mnt)_2^{n-}$, or 1,2-diperfluoromethylethylenedithiolato complexes, $M(scf)_2^{n-}$.

(i) TCNQ	$(Et_4N)_2[Ni(mnt)_2]$	748	765	849
	$(Et_4N)_2[Cu(mnt)_2]$	747	762 sh	848
	$(Et_4N)_2[Zn(mnt)_2]$	749	763 sh	850
(ii) TCNE	$(Et_4N)_2[Ni(mnt)_2]$	polybanded		374 -470
	$(Et_4N)_2[Cu(mnt)_2]$	polybanded		390*-470
	$(Et_4N)_2[Zn(mnt)_2]$	polybanded		420*-470
	$(Et_4N)_2[Pt(mnt)_2]$	polybanded		376 -470
	$(Et_4N)_2[Ni(scf)_2]$	polybanded		366 -470

* lower wavelength absorption dominated by bands due to unchanged complex or excess of quinone.

The stoichiometry of interaction was investigated for several maleonitriledithiolato complexes, in each case with Q as acceptor. This quinone was chosen since its anion has one band (580-590 mμ) which occurs in a region where neither the donors used nor the neutral quinone molecule absorb significantly. Absorbance of mixed donor-acceptor solutions are reported in Table IV. The results indicate a 1:1 stoichiometry showing that in the simple

model used to represent these systems the equilibrium lies at, or very close to, the right-hand side. Unfortunately these results cannot be checked directly against the molar extinction coefficient of Q^- in dichloromethane solution since this quantity could not be determined. $TMPD^+$ absorbs in the same region as Q^-, so TMPD cannot be used to generate Q^- at known concentration; weaker donors than TMPD do not generate Q^- in dichloromethane; and all the alkali metal iodides are too insoluble in dichlomethane for this approach to be used. However it is possible to determine the extinction coefficient for Q^- in acetone using iodide as donor, and to compare this with that using $Ni(mnt)_2^{2-}$ as donor in the same solvent. The agreement is reasonable, and the extinction coefficient for Q^- generated by $Ni(mnt)_2^{2-}$ is similar in acetone and in dichloromethane (Table V).

Average molar extinction coefficients, calculated assuming 1:1 stoichiometry from the results given in Table IV, are given for each donor complex in Table VI. The overall consistency of values in Table V and VI strongly supports the 1:1 stoichiometry indicated by Table IV.

Although most of this investigation has been devoted to maleonitriledithiolato complexes we have examined

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

[8] J. B. Raynor, to be published.

Table III. Comparison of new bands for mixed solutions prepared from bis-maleonitriledithiolatonickel(II), Ni(mnt)$_2^{2-}$, or from bis-(1,2-diperfluoromethylethylenedithiolato)nickel(II) Ni(scf)$_2^{2-}$, and organic acceptors with those for established acceptor anions; N = no new bands observed.

		Donor	Solvent	Bands			Ref.
(i)	TCNQ	$(Et_4N)_2[Ni(mnt)_2]$	CH_2Cl_2	748	765	849	—
		TMPD	MeOH	744		844	10
		I^-	THF	750	772	835	11
(ii)	Q	$(Et_4N)_2[Ni(mnt)_2]$	CH_2Cl_2	540		585	—
		$(Et_4N)_2[Ni(scf)_2]$	CH_2Cl_2	544		586	—
		TMPD	CH_2Cl_2	(~540 sh)		(~580 sh)	*
		$(Et_4N)_2[Ni(mnt)_2]$	acetone	552		594	—
		phenylenediamine	acetone	550		595	—
		I^-	acetone	554		593	—
(iii)	*p*-chloranil	$(Et_4N)_2[Ni(mnt)_2]$	CH_2Cl_2	‡		450	—
		$(Et_4N)_2[Ni(mnt)_2]$	acetone	‡		447	—
		$(Et_4N)_2[Ni(scf)_2]$	acetone	419		446	—
		TMPD	acetone	419		446	—
		$(Et_4N)_2[Ni(scf)_2]$	MeOH	424		452	—
		TMPD	MeOH	426		452	10
		$(Et_4N)_2[Ni(scf)_2]$	MeCN	420		447	—
		TMPD	MeCN	422		448	10
(iv)	TCNE	$(Et_4N)_2[Ni(mnt)_2]$	CH_2Cl_2	374	to	470 §	—
		TMPD	CH_2Cl_2	370	to	470 §	—
		TMPD	aq, MeOH, MeCN	370	to	470 §	10
(v)	2,5-dichloro-*p*-benzoquinone	$(Et_4N)_2[Ni(mnt)_2]$	CH_2Cl_2		N		—
		$(Et_4N)_2[Ni(scf)_2]$	CH_2Cl_2	418		442 sh	—
		$(Et_4N)_2[Ni(scf)_2]$	acetone	420		450 sh	—
		$(Et_4N)_2[Ni(scf)_2]$	MeOH	415		442 sh	—
		TMPD	aq			444	10
(vi)	2,6-dichloro-*p*-benzoquinone	$(Et_4N)_2[Ni(mnt)_2]$	acetone		N		—
		$(Et_4N)_2[Ni(scf)_2]$	acetone	426		450	—
		I^-	acetone	425		450	—
		$(Et_4N)_2[Ni(scf)_2]$	MeOH	425		(445-450)	—
		TMPD	MeOH	427		453	10
(vii)	*p*-benzoquinone	$(Et_4N)_2[Ni(mnt)_2]$ $(Et_4N)_2[Ni(scf)_2]$	CH_2Cl_2, acetone		N		—
(viii)	toluquinone	$(Et_4N)_2[Ni(mnt)_2]$ $(Et_4N)_2[Ni(scf)_2]$	CH_2Cl_2, acetone		N		—

* Overlaps TMPD$^+$ spectrum; ‡ $[Ni(mnt)_2]^{2-}$ has a strong absorption in this region; § polybanded at 9-10 mμ intervals; sh = shoulder.

Table IV. Absorbances at 585 mμ (OD$_{585}$) of dichloromethane solutions of bis-maleonitriledithiolato complexes, M(mnt)$_2^{2-}$, and 2,3-dichloro-5,6-dicyano-*p*-benzoquinone, Q, at 25.0°. Concentrations quoted in column headings are the values before reaction.

10^4 $[Ni(mnt)_2^{2-}]$ *M*	10^4 [Q] *M*	OD$_{585}$	10^4 $[Cu(mnt_2^{2-}]$ *M*	10^4 [Q] *M*	OD$_{585}$
1.92	0.38	0.24	1.92	0.38	0.25
1.92	1.15	0.62	1.92	1.15	0.70
1.92	1.92	1.01	1.92	1.92	1.09
1.92	2.70	0.98	1.92	2.70	1.17
1.92	3.08	1.09	1.92	3.47	1.09
1.92	3.47	0.97	1.92	3.84	1.19
1.92	3.84	1.11	1.92	4.23	1.11
1.92	81	0.97	1.92	8.07	1.09
3.84	0.77	0.38			
3.84	1.54	0.78			
3.84	2.31	1.16			
3.84	3.08	1.53			

10^4 $[Pd(mnt_2^{2-}]$ *M*	10^4 [Q] *M*	OD$_{585}$
1.54	1.85	0.96

10^4 $[Zn(mnt)_2^{2-}]$ *M*	10^4 [Q] *M*	OD$_{585}$
1.92	5.70	1.15

a variety of inorganic compounds to see which are able to donate electrons to 2,3-dichloro-5,6-dicyano-*p*-benzoquinone to generate Q, generally in dichloromethane. Many mixed halide-phosphine complexes, including $[Pt(PPh_3)_3F](HF_2)$, *cis*-$Ni(PPh_3)_2Cl_2$, $Co(PPh_3)_2Cl_2$, $Pd(PPh_3)_2Cl_2$ (though not $Au(PPh_3)Cl$), and carbonylphosphine compounds, *e.g.* *cis*-$Ru(CO)_2(PPh_3)_2Cl_2$, $Fe(CO)_3(PPh_3)_2$, and $Ni(CO)_2(PPh_3)_2$ do generate Q^-. The simple carbonyls $M(CO)_6$, M=Cr, Mo, W, do not. With metal-phosphine-halides, $M(PR_3)_2X_2$, electron transfer often takes place from the *cis* isomer but not from the *trans*. In many cases only a relatively small amount of Q^- is generated, indicating that the equilibria $D+A \rightleftharpoons D^+A^-$ or $D.A \rightleftharpoons D^+ + A^-$ lie towards the left. Thus the addition of between 5 and 20×10^{-3} *M* solutions of Q in dichloromethane to 1.15×10^{-2} *M* cis-bis-(tri-n-buthylphosphine)platinum(II) chloride gives absorbances of about 0.1 to 0.2 at 585 mμ.* Using the molar extinction coefficient for Q^- calculated earlier, and assuming the equilibrium to be $D.A \rightleftharpoons D^+ + A^-$, one can calculate

(*) Absorbances due to Q^- formation can only be estimated approximately here, since at these relatively high concentrations of reactants absorbances due to unchanged donor and acceptor separately interfere.

Table V. Determination of the molar extinction coefficient, ε_{585} or ε_{595}, in dichloromethane and acetone respectively, of the 2,3-dichloro-5,6-dicyano-*p*-benzoquinone anion, Q^-

Donor	Solvent	$10^4[Q^-], M$	OD_{595} OD_{585}	ε_{595} ε_{585}
I^-	acetone	2.83	1.61	5700
$(Et_4N)_2[Ni(mnt)_2]$	acetone	2.91	1.82	6200
$(Et_4N)_2[Ni(mnt)_2]$	CH_2Cl_2	1.94	1.19	6100

Table VI. Estimates of the molar extinction coefficient, ε_{585}, for the 2,3-dichloro-5,6-dicyano-*p*-benzoquinone anion, Q^-, in dichloromethane from Table IV results.

Complex	ε_{585}
$(Et_4N)_2[Ni(mnt)_2]$	5300
$(Et_4N)_2[Cu(mnt)_2]$	6000
$(Et_4N)_2[Zn(mnt)_2]$	6000
$(Et_4N)_2[Pd(mnt)_2]$	6200

Table VII. Solvent effects on the visible absorption bands of the 2,3-dichloro-5,6-dicyano-*p*-benzoquinone anion. N = no evidence for Q^- in these cases; I = donor insoluble; E_T values from reference 8.

Solvent	E_T	Donor $(Et_4N)_2[Ni(mnt)_2]$		$[(PPh_3)_3PtF](HF_2)$		*cis*—$[(PPh_3)_2PtCl_2]$	
$MeNO_2$	46.3	546	587	544	583	547	587
MeCN	46.0	548	590	546	586	549	589
Acetone	42.2	552	594	554	594		
CH_2Cl_2	41.1	544	585	542	582		
PhCl	37.5	I		(540)	585	N	
C_6H_6	34.5	I		N		N	

an equilibrium constant $K \cong 10^{-4}$ M^{-1} for this case. Alternatively if the equilibrium $D+A \rightleftharpoons D^+ + A^-$ be assumed, then $K \cong 10^{-6}$. On either assumption the contrast with the $Ni(mnt)_2^{2-}$ case, where $K \cong 1$, is clear.

No system studied here gave absorption bands which could be unequivocally assigned to a charge-transfer band of a complex D . A. Absorption bands of the reaction components obscure much of the region where such absorption would be expected. However in view of the similarity of our systems to others where charge-transfer bands have been observed we feel it justifiable to interpret our results in terms of such intermediate D . A complexes.

Solvent effects on acceptor anion spectra were briefly studied. The results in Table VII, as well as relevant results included in Table III, show that solvent effects are small, and moreover do not correlate with the standard spectroscopically-based solvent parameter E_T. The significant feature of Table VII is not the variation of wavelengths of maximum absorption with solvent, but rather the non-appearance of the anion spectrum in poor solvents such as benzene, where there will be negligible stabilisation of D^+ and A^- by solvation (*cf.* Introduction).

In all the preceding cases electron transfer has taken place from an inorganic donor to an organic acceptor. We have also sought examples of the converse process, donation from an organic donor such as TMPD to an inorganic acceptor. Two examples are already well established - oxygen with TMPD gives $TMPD^+O_2^-$, while electron transfer also occurs between $[Ni(S_2C_2(CF_3)_2)_2]^\circ$ and pyrene or perylene.[9] Working in acetone, which we have found easier to free from oxygen than dichloromethane, we have also generated $TMPD^+$ by the action of acceptors $HgCl_2$, $VO(acac)_2$, and *cis*-$Pt(py)_2Cl_4$ on TMPD.

The expected electron transfer takes place between $Ni(mnt)_2^{2-}$ and $HgCl_2$, as shown by our observation of the characteristic e.s.r. signal due to the nickel(III) complex $Ni(mnt)_2^-$ in mixed dichloromethane solutions of these inorganic donor and acceptor species.

Experimental Section

The transition metal-dithiolene complexes were kindly supplied by Dr. J. B. Cornell. Other metal complexes were prepared by standard literature procedures. Organic acceptors were obtained from Koch-Light. All solvents were dried and purged with nitrogen before use.

Visible absorption spectra were run on a Unicam SP800A, Beckmann DK-2A, or Beckmann DB-G, spectrophotometer. The wavelength calibrations of these instruments were periodically checked using standard holmium and didymium glass filters. In the stoichiometric experiments solutions were thermostatted at 25.0° in the cell holder of the SP800A, through which was circulated water from a constant temperature bath controlled by contact thermometer and relay.

Electron spin resonance measurements were obtained on a Varian Associates E3 spectrometer.

Acknowledgements. We thank the Royal Society for a grant to purchase the Unicam SP800A spectrophotometer, the Science Research Council for a maintenance grant (to J. S.), and Dr. J. B. Raynor for obtaining and interpreting the e.s.r. spectra.

(9) R. D. Schmitt, R. M. Wing, and A. H. Maki, *J. Amer. Chem. Soc.*, *91*, 4394 (1969).

(10) R. Foster and T. J. Thomson, *Trans. Faraday Soc.*, *58*, 860 (1962).

(11) R. Foster and T. J. Thomson, *Trans. Faraday Soc.*, 59, 296 (1963).