Electronic Spectral Studies of Dithio- and Perthio-carboxylato-nickel(II) Complexes

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The electronic spectra of a large series of nickel(II) complexes containing dithio- and perthio-carboxylate ligands have been measured and correlation of these spectra with known structures made. The spectra of adducts formed between these complexes and pyridine are reported. A general spectral comparison is made of the dithio- and perthio-carboxylate complexes with those containing dialkylphosphorodithioates, xanthates, and dithiocarbamates.

QUADRATIC [NiS_4] chromophores, as present in NiL_2 complexes, where L = $R{-}CS_2^-$ or $R{-}CS_2S^-$,[1-3] differ markedly, both in stereochemistry and electronic spectra, from [NiS_4] chromophores present in dtc, xant, or ept complexes (abbreviations used: ept = *OO*-diethyl phosphorodithioate, xant = xanthate, dtc = dialkyl dithiocarbamate). The latter show simple quadratic (or better, rectangular) monomeric structures having Ni–S: 2·16—2·24 Å and ligand ' bites ' of *ca.* 2·80 Å.[4-7] Their spectra may be classified [8] into *d–d* bands ($\bar{\nu}_1$ *ca.* 15—18, $\bar{\nu}_2$ *ca.* 19—23 kK, both having log ε *ca.* 2), charge transfer bands (starting at 25—26 kK with log ε *ca.* 3—3·5) and ligand internal transitions in the far-u.v. Dithiocarboxylates and perthiocarboxylates, however, yield different stereochemistries.[9-12] Their complicated visible and u.v. spectra defy any simple classification and rationalization in terms of current ligand field, or empirical MO models. In some respects (very low $\bar{\nu}_1$ *d–d* transition, several intense visible bands, large ' bite ' angle, and Ni–S *ca.* 2·16 Å in perthiocarboxylate chelate rings), this group of complexes resembles 1,2-dithiolates, such as $Ni(mnt)_2^{2-}$.[13-14] However, spectral similarity between four- and five-membered dithio- and perthiocarboxylato-chelate rings, lack of extensive conjugation within chelate rings involving disulphide linkages, absence of reversible multistage redox transformations, and marked differences between nickel dithiocarboxylates with different organic groups, prevent any interpretative approach analogous to that of 1,2-dithiolates. Satisfactory interpretation can probably be achieved only *via* a full MO treatment. Until the latter becomes available in standard form, we present a detailed account of the properties of these systems in order to provide an experimental foundation for future theoretical treatment. The preparative work, and recent *X*-ray structural data on some representative complexes, already allow some generalizations to be made.

EXPERIMENTAL

Preparations.—Dithiocarboxylic acids and their sodium salts were obtained following known procedures: MeCSSH, dtaH;[15] Me_3CCSSH, dtpvH;[16] $PhCH_2CSSH$, dtpaH;[17]

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PhCSSH, dtbH;[18] p-MeC$_6$H$_4$CSSH, dttH.[19] The complexes Ni(dtb)$_2$,[20] Ni(dtt)$_2$,[21] and Ni(dtpa)$_2$ [22] were prepared as in the literature.

Bis(dithioacetato)nickel(II).—An excess of NiCl$_2$,6H$_2$O (2·5 g, 10·5 mmol) in ethanol (25 ml) was added to a freshly prepared solution of dtaH (1 g, 10·7 mmol) in ether (30 ml). A precipitate formed immediately and after being left to stand, was filtered off. Recrystallization from CS$_2$ gave 1·10 g (88% yield) of red-black Ni(dta)$_2$ (m.p. 134—136°) (Found: C, 20·1; H, 2·65; Ni, 24·15; S, 53·05. C$_4$H$_6$NiS$_4$ requires C, 19·9; H, 2·45; Ni, 24·4; S, 53·2%).

A preparation of Ni(dta)$_2$ has been described previously,[23] and involves reaction of 2 : 1 mole proportions of dtaNa and NiCl$_2$,6H$_2$O in water. Following this method we obtained a product, which chemical analyses, m.p., and visible–u.v. spectra showed to be different from the expected Ni(dta)$_2$. The dark material which precipitated from the aqueous reaction mixture was dried and recrystallized from benzene. Bright black crystals were obtained, the analysis and physical properties of which are very similar to those of the trinuclear compound described below. *X*-Ray analysis showed [24] that this compound is a polymorphic form of (dta)$_3$Ni$_3$(S$_3$CMe). The crystal structure is presently being refined.

Trithio-orthoacetato[dithioacetatonickel(II)].—This was obtained by recrystallization of Ni(dta)$_2$ from a CS$_2$–EtOH mixture (m.p. 184°, with decomposition) (Found: C, 17·05; H, 2·2; Ni, 30·6; S, 49·85. C$_8$H$_{12}$Ni$_3$S$_9$ requires C, 16·75; H, 2·1; Ni, 30·75; S, 50·35%). A trinuclear structure and the presence of the unusual trithio-orthoacetato ligand in the complex have been shown by *X*-ray analysis. The structure of the compound is shown in Figure 2.

Addition of ethanol to a Ni(dta)$_2$ solution in CS$_2$ changes the electronic spectrum of Ni(dta)$_2$ into that of (dta)$_3$-Ni$_3$(S$_3$CMe). Solutions of the last mentioned complex in common organic solvents are stable, as shown by their electronic spectra. These solutions are unaffected by addition of an excess of pyridine.

Bis(dithiopivalato)nickel(II).—A solution in ether (30 ml) of dtpvH (1 g, 7·5 mmol) was added to a solution of NiCl$_2$,6H$_2$O (1 g, 8·4 mmol) in ethanol (20 ml). The deep green reaction mixture was evaporated to dryness, the residue extracted with n-hexane and crystallized from this solvent below room temperature. Yield 0·9 g (75%) of dark reddish green crystals (m.p. 158—160°) (Found: C, 36·25; H, 5·75; Ni, 18·15; S, 38·7. C$_{10}$H$_{18}$NiS$_4$ requires C, 36·95; H, 5·55; Ni, 18·1; S, 39·4%).

Mixed Dithio-perthio-carboxylato-nickel(II) *Complexes*, (RCS$_2$)(RCS$_3$)Ni.—These complexes may be obtained in the following three ways. (*i*) By oxidation of dithiocarboxylates (formed by dismutation of the corresponding monothiocarboxylato-complexes) with sulphur, *e.g.* Ni(dtb)-(dtbS);[20,21] (*ii*) by partial desulphuration of bis-perthiocarboxylato-complexes using triphenylphosphine, *e.g.* Ni-(dtt)(dttS);[11] (*iii*) by mixing equimolecular quantities of bisdithio- and bisperthio-carboxylates of nickel(II) in inert organic solvents, as in the preparation of Ni(dtpv)(dtpvS). Although the last mentioned complex has not been isolated in the solid state, its existence in solution has been proved by n.m.r. [two inequivalent CH$_3$ frequencies at 1·31 and 1·58 p.p.m. (Me$_4$Si standard)] [25] and by electronic spectra (see below).

Mixed dithio-perthio-carboxylato-zinc(II) complexes appear to be unstable. Desulphuration of bis-perthiocarboxylato-complexes in this case is not stepwise, but leads directly to the bis-dithiocarboxylato-derivatives. Instability also occurs with nickel(II) for aliphatic ligands (where, apart from dtpvS$^-$, perthiocarboxylates cannot be formed). Thus, the existence of mixed dithio-perthiocarboxylato-complexes is limited to nickel(II) with aromatic dithio- and perthio-carboxylato-ligands, Ni(dtpV)(dtpVS) being the only known exception.

Bis(perthiocarboxylato)nickel(II) *Complexes*.—These have already been extensively described.[3] Aromatic perthiocarboxylato-complexes are more stable than aliphatic.

Pyridine Adducts.—Except for the trinuclear (dta)$_3$Ni$_3$-(S$_3$CMe), 1 : 2 adducts are formed in all cases from a slight excess of pyridine in non-co-ordinating solvents. Ni(dtb)$_2$-(py)$_2$ and Ni(dtpa)$_2$(py)$_2$ were reported previously.[1] Although Ni(dtt)$_2$(py)$_2$, Ni(dta)$_2$(py)$_2$, and Ni(dtpv)$_2$(py)$_2$ are formed in solution, as shown by their spectra, no attempts have been made to isolate them in the solid state.

Bis(dithioacetato)zinc(II).—This was obtained by mixing aqueous solutions of dtaNa and ZnCl$_2$. A yellow precipitate was formed immediately and it was recrystallized from benzene (Found: C, 47·7; H, 3·75; S, 31·85. C$_{16}$H$_{14}$S$_4$Zn requires C, 48·05; H, 3·55; S, 32·05%).

The other zinc(II) complexes were prepared as in the literature: Zn(dtpa)$_2$,[26] Zn(dtb)$_2$,[21] Zn(dtt)$_2$,[21] Zn(dtbS)$_2$,[3] Zn(dttS)$_2$,[3] and Zn(dtpvS)$_2$.[13]

Magnetic Measurements.—These were performed by both the Gouy and the Faraday methods, in the liquid nitrogen to room temperature range. Almost all the complexes exhibited some degree of paramagnetism (sometimes up to 2—3 B.M.), which was almost temperature independent, strongly field dependent, non-reproducible, and of decreasing intensity on repeated recrystallization. Extrapolation of Faraday measurements to $1/H \longrightarrow 0$ shows that permanent paramagnetism is absent in these complexes, although they rarely become diamagnetic. We conclude that nickel(II) dithio- and perthio-carboxylates are diamagnetic low-spin nickel(II) chromophores, but are frequently accompanied by ferromagnetic impurities from which they cannot easily be freed by recrystallization. ^{1}H N.m.r. measurements of solutions of Ni(dtb)$_2$, Ni(dttS)$_2$, and Ni(dtbS)$_2$ in CS$_2$ confirm diamagnetism, showing normal phenyl resonance without paramagnetic shifts.[11,25] This is in agreement with earlier measurements [1,3] on the analogous dithio- and perthio-toluato-complexes.

Solubility and Molecular Measurements.—All the complexes have low–medium solubilities in non-polar or weakly polar organic solvents. The best solvent is CS$_2$, followed by CHCl$_3$, CCl$_4$, benzene, toluene, paraffins (order of magnitude *ca.* 1—3 × 10^{-3}M at room temperature). They are much less soluble in polar solvents (alcohols, acetone, DMF, CH$_3$CN) and insoluble in water. Pyridine dissolves

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them but with formation of 1 : 2 adducts. Higher solubilities are found for Ni(dtpv)$_2$ and Ni(dtpvS)$_2$ in benzene, CS$_2$, *etc.*, and these were the only complexes for which molecular weight measurements could be performed. For Ni(dtpv)$_2$ M was concentration dependent (osmometry, Mechrolab 301) (Figure 1). This initially shows $C \propto (1 - \alpha)/\alpha^2$ (α = degree of dimer dissociation, with the slope K(dimerization) $= (1 - \alpha)/4C\alpha^2 = 5{\cdot}5$ l mol^{-1}, in benzene at 37°. Nonlinearity of the graph at higher concentrations implies appreciable formation of higher polymers at degree of total polymerization $\gtrsim 0{\cdot}3$.

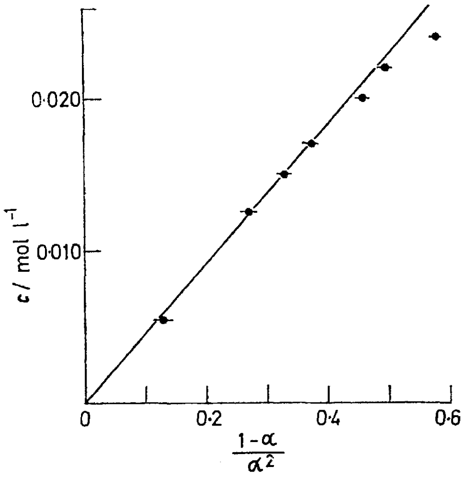

FIGURE 1 Plot illustrating the dimer formation of Ni(dtpV)$_2$ in benzene

RESULTS

Structures and Electronic Spectra.—The present work characterizes several compounds which have been previously prepared but not extensively investigated spectroscopically, plus some new ones.

The Table reports the electronic spectra of the nickel(II) complexes. Data on some analogous zinc(II) complexes and on the free ligands, LH and L$^-$, are reported for comparison and as an aid in preliminary assignments. Spectra were recorded on a Beckmann DK 1A machine and copies of them have been deposited in Supplementary Publication No. 20750 (8 pp.).*

All the reported nickel(II) dithio- and perthio-carboxylates may be described as containing a basically square planar low-spin [NiS$_4$] chromophore. However, there is evidence from the data that the [NiS$_4$] chromophore exhibits a wide range of spectral properties. The aromatic or aliphatic character of the ligand substituents, the order of the chelated ring, *etc.*, appear to influence the spectral behaviour. Since this influence parallels the numerous types of molecular structure found, it is useful to look for some correlations between spectra and structural behaviour. For purpose of classification, the following groups may be distinguished (to which the spectra in the Table are referred).

(I) *Dithiocarboxylatonickel*(II) *Complexes.*—(a) R = *Aryl.* Structures are essentially monomeric quadratic [NiS$_4$] chromophores, although intermolecular interactions may lead to polymeric association with axial five- or six-co-ordination as in the case of Ni(dtb)$_2$, in which loose axial contacts of 3·1 Å bridge the molecules into groups of three.[9] However, these interactions are weak, and do not sensibly affect the spectra. Solution and solid state spectra are essentially similar, showing a very intense band at *ca.* 17 kK (log ε *ca.* 4), and, presumably, a *d–d* transition of *ca.* 13 kK (log ε *ca.* 2·8) (Table a).

(b) R = *Alkyl.* Solid complexes occur as polynuclear units. In dimeric Ni$_2$(dtpa)$_4$ all four ligands are bridging.[10] A Ni–Ni distance of 2·56 Å and 'inward' out-of-plane distortion of 0·13 Å are consistent with significant Ni–Ni bonding. In the electronic spectrum there are strong charge transfer transitions around 20 kK (log ε *ca.* 3·0—3·3) and 30·6 kK (log ε *ca.* 4·2), preceded by a *d–d* absorption region between 13 and 15 kK (log ε *ca.* 1·3—1·7). Crystal polarized spectra contain several components and this multiplicity has been shown to be consistent with doubling of the *d*-levels caused by Ni–Ni interaction in the dimer unit.[27] A similar bridged structure is presumably also present in Ni(dta)$_2$. From nickel salts and the dithioacetate ion, further polynuclear complex species can be obtained, following partial decomposition of the dithioacetate ligand. The trinuclear compound (dta)$_3$Ni$_3$(S$_3$CMe) has recently been shown by Bonamico and his co-workers [24] to contain a trinuclear nickel cluster with Ni–Ni distances of *ca.* 3 Å. Three MeCS$_2^-$ ligands link the cluster by providing two-co-ordinated sulphur atom below the Ni$_3$ plane, while a MeCS$_3^{3-}$ trithio-orthoacetate ligand places its sulphur atoms above the same plane in a bridging position between the nickel atoms (Figure 2). Therefore each nickel atom is surrounded, in roughly quadratic co-ordination, by four sulphur atoms (two from a dithioacetate and two, bridging, from MeCS$_3^{3-}$), while the whole molecule has approximate threefold symmetry.

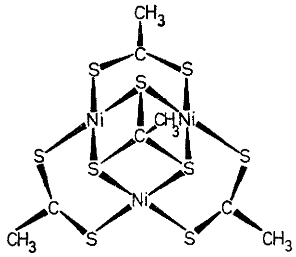

FIGURE 2 Structure of (dta)$_3$Ni$_3$(S$_3$CMe) (ref. 24)

(c) *Dimer association.* Ni$_2$L$_4$ (L = R–CS$_2^-$, R = aliphatic) does not survive in solution. The spectra of fresh solutions of Ni$_2$(dtpa)$_4$, or Ni$_2$(dta)$_4$, resemble those of the parent solids. In nonpolar organic solvents (*e.g.* C$_6$H$_6$, CS$_2$, CHCl$_3$ but not alcohols) the spectra change rapidly with time, giving, finally, three close maxima of intermediate intensity (log ε *ca.* 2·7—2·9) in the *d–d* region (*ca.* 15·0—16·7—17·2 kK). Charge transfer bands similar to those of (Ib) [main band at 30·6 kK (log ε *ca.* 4·3) with shoulder at *ca.* 20 kK] are also observed. A similar spectrum is obtained from aged solutions of Ni(dtpa)$_2$, Ni(dta)$_2$, and fresh solutions of Ni(dtpv)$_2$ in CS$_2$ and other nonpolar solvents [behaviour in benzene solutions may be complicated by association equilibria, see (Id)]. For Ni(dtpv)$_2$, mole-

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* For details of Supplementary Publications see Notice to Authors No. 7, *J.C.S. Dalton*, 1972 Index issue (items less than 10 pp. are supplied as full-sized copies).

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Electronic spectra [maxima in kK and (log ε); shoulders in parentheses] of dithio- and perthio-carboxylates

(a)

Free ligands				Nickel(II) complexes: spectral type Ia and related zinc(II) complexes				Nickel(II) complexes: spectral type II			Nickel(II) complexes: spectral type III			Tentative assignment
dtbH Ether	dtb$^-$ Water	dttH Ether	dtt$^-$ Water	Ni(dtb)$_2$ [a]	Zn(dtb)$_2$	Ni(dtt)$_2$ [b]	Zn(dtt)$_2$	Ni(dtpv)(dtpvs)	Ni(dtb)(dtbS) [c]	Ni(dtt)(dttS) [d]	Ni(dtpvS)$_2$	Ni(dtbS)$_2$	Ni(dttS)$_2$	Compound Solvent
				13·1(2·84)		13·3$_5$(2·85)		(15·3)(2·07)	(13·2)(1·86)	13·35(1·74)	11·8(1·49)	11·8(1·66)	12·0(1·71)	Ligand-field(?)
				(15·7)(3·40)		15·5(3·42)					(17·4)(2·79)	(15·6)(2·72)	(15·6)(2·66)	Characteristic visible bands
				16·8(3·96)		16·9(3·97)		21·7(3·84)	19·0(3·90)	19·1(4·00)	20·0(3·41)	18·0(3·43)	18·0(3·48)	
				(18·2)(3·55)		(18·5)(3·52)								
19·0(1·83)	20·8(2·15)	19·0(1·72)	21·7(2·22)		21·0(1·50)		21·3(1·78)							$n \longrightarrow \pi$(C=S)
				(23·4)(3·07)	27·2(4·03)	(23·9)(3·35)	27·8(4·03)	25·0(3·64)	22·8$_5$(3·57)	23·0(3·70)	26·0(3·55)	23·9(4·04)	23·5(4·15)	Charge transfer
30·0(3·66)	28·2(3·70)	32·4(3·90)	28·7(3·67)	29·2(4·88)	30·4(4·56)	28·5(4·91)	28·6(4·70)	31·2(4·50)	29·7(4·73)	29·3(4·82)	31·2(4·34)	29·3(4·59)	28·8(4·63)	Ligands π–π^* plus possible charge transfer
33·7(3·98)	34·1(3·63)		32·1(2·85)	34·1(4·27)		34·4(4·16)	(32·2)(3·21)	35·7(4·32)	34·0(4·27)	34·4(4·25)	39·0(4·15)	(35·0)(4·24)	(35·0)(4·25)	
43·5(3·67)	40·5(3·55)	43·4(3·68)	40·5(3·74)											Ligands π—π^*

(b)

Free ligands				Nickel(II) complexes: spectral type Ib and related zinc(II) complexes							Nickel(II) complexes: spectral type Ic			Tentative assignment
dtaH Ether	dta$^-$ Water	dtpaH Ether	dtpa$^-$ Water	(dta)$_3$Ni$_3$(S$_3$CCH$_3$)	Ni$_2$(dta)$_4$	Ni$_2$(dta)$_4$ Reflectance	Ni$_2$(dtpa)$_4$	Ni$_2$(dtpa)$_4$ Reflectance	Zn(dta)$_2$	Zn(dtpa)$_2$	Ni(dta)$_2$	Ni(dtpa)$_2$	Ni(dtpv)$_2$	Compound Solvent
				(15·0)(2·25)	(13·9)(1·46)	(13·3)	(13·0)(1·34)	(13·1)			15·3(2·70)	14·8$_8$(2·75)	14·9$_3$(2·96)	Ligand-field bands
				(17·5)(2·88)	(14·8)(1·57)	(14·2)	(14·7)(1·65)				16·6(2·80)	16·3$_4$(2·78)	16·3$_9$(2·90)	
						(18·5)		(18·2)			17·5(2·84)	17·2$_4$(2·90)	17·6$_4$(2·98)	
19·6(1·26)	22·4(1·62)	20·8(1·36)	20·8(1·65)							24·5(1·83)				$n \longrightarrow \pi$ (C=S)
				22·4(3·48)		21·2	19·8(3·07)	(19·8)			20·1(3·16)	19·8(3·30)	20·0(3·35)	Charge transfer
				(24·1)(3·51)	20·1(2·95)						24·1(3·08)	24·0(3·28)	24·0(3·12)	
				27·8(3·94)	(26·0)(3·18)			21·7						
34·1(4·05)	30·0(4·19)	34·1(3·74)	29·4(3·90)	(32·3)(4·25)	30·9(4·12)		30·7(4·18)		27·0(3·80)	28·8(3·84)	30·6(4·24)	30·5(4·35)	30·3(4·45)	Ligands π—π^* bands
(43·1)(3·30)	(41·7)(3·38)	40·6(3·40)	40·8(3·34)	36·2(4·51)	36·0(4·34)		35·3(4·40)				35·8(4·30)	35·3(4·29)	35·3(4·27)	
48·8(4·01)	(46·9)(4·04)	>47	>47	(39·1)(4·31)	(38·0)(4·15)		(37·7)(4·32)		33·0(2·47)	37·9(2·91)	(39·2)(3·89)	(38·3)(4·15)		

(c)

Free ligands		Nickel(II) complexes: spectral type Id		Tentative assignment	Nickel(II) complexes: spectral type Ie (pyridine adducts)							Tentative assignment
dtpvH Ether	dtpv$^-$ Water	Ni(dtpv)$_2$	Ni(dtpv)$_2$ Reflectance	Compound Solvent	Ni(dta)$_2$-(py)$_2$ Benzene or Pyridine	Ni(dtpa)$_2$-(py)$_2$ [e]	Ni(dtpv)$_2$-(py)$_2$	Ni(dtb)$_2$-(py)$_2$ [f] Benzene	Ni(dtt)$_2$-(py)$_2$	Ni(dtb)(dtbS) (py)$_2$ Pyridine	Ni(dtbS)$_2$-(py)$_2$ Pyridine	Compound Solvent
		15·1$_1$(3·15)	15·4$_6$	Ligand-field bands	10·5$_3$(1·53)	10·3(1·60)	10·4$_3$(1·55)	10·5(1·60)	10·5(1·60)	10·5(1·57)	10·5	$^3A_{2g} \longrightarrow {}^3T_{2g}(O_h)$
		16·1$_6$(3·18)	(15·9$_2$)		16·6$_7$(1·76)	16·7(1·81)	16·6$_7$(1·81)	(17·2)(2·45)	(17·2)(2·40)	(18·2)(2·72)	(18·2)	$^3A_{2g} \longrightarrow a^3T_{1g}(O_h)$
		17·1$_8$(3·12)	(17·1$_5$)					19·1(2·62)	19·1(2·58)	19·2(2·78)	19·2	Charge transfer (?)
20·4(1·24)	21·7(1·54)			$n \longrightarrow \pi$(C=S)	(22·0)(2·58)	(22·0)(2·68)	(22·2$_3$)(2·58)	24·9(3·83)	24·9(3·85)	(24·4)(3·77)	24·5	$^3A_{2g} \longrightarrow b^3T_{1g}(O_h)$ Charge transfer (?)
		20·1(3·47)	20·6	Charge transfer	22·9(3·80)	(22·9)(3·85)	22·9(3·80)					
33·3(3·83)	29·4(4·10)	30·5(4·30)	30·6	Ligands π—π^* bands								
(44·8)(3·55)	(40·8)(3·35)											
48·1(3·90)	46·1(3·97)											

Reflectance: 12·0$_5$, 16·4 kK. [b] Reflectance: 12·6$_5$, 16·3, (17·7), and (21·6) kK. [c] Reflectance: 12·2, (17·9), 18·2$_5$, 21·3, 29·8, and 33·9 kK. Reflectance: (12·6), (18·2), 18·9, and (21·7) kK. [e] Single crystal spectrum: 16·5$_3$, 21·7$_4$, and 24·1 kK. [f] Reflectance: 16·4, 19·5, and 22·5 kK.

cular weight measurements showed that the solute is monomeric. It also gives spectra of type (Ic), therefore we assign a structure of type (Ic).

(d) Concentrated benzene solutions of Ni(dtpv)$_2$ give molecular weights of $n > 1$, showing the presence of dimers, or higher polymers. The spectra of these solutions are similar to those of (Ic). Of the three bands in the visible region, that at *ca.* 16·0 kK becomes the most intense, its intensity increasing to log ε *ca.* 3·2. The crystal structure of Ni(dtpv)$_2$ consists of pairs of monomeric chelate units Ni(dtpv)$_2$ linked by loose bonding (2·7 Å) of each nickel to one sulphur of the other monomer unit.[24] This interaction causes an out of plane distortion of the nickel (0·4 Å) and of the sulphur (0·7 Å) which interact. Such association differs from that in Ni$_2$(dtpa)$_4$ in that there are no bridging ligands and less marked spectral changes accompanying association. However, the interaction between monomers is stronger than in Ni(dtb)$_2$ (where it does not lead to detectable spectra changes and does not survive at all in solution).

(e) *Pyridine adducts.* All dithiocarboxylato-nickel(II) complexes (except the trinuclear one), readily form 1 : 2 adducts with pyridine, assumed to contain *trans*-[NiS$_4$N$_2$] chromophores. The spectra fit pseudo-octahedral, high spin nickel(II) patterns and there are no significant differences between dta, dtb, or dtpv ligands. Assignments in the Table (c) are consistent with Δ_{av} = 10·1—10·4 kK, B = 0·7 kK [compare Δ_{av} = 9·0—9·3 kK for Ni(dtpi)$_2$(py)$_2$,[28] but Δ_{av} = 9·3—10·2 kK for Ni(exan)$_2$(py)$_2$]. Charge transfer bands are present at low frequencies (23—24 kK generally, and 19 kK in dithio- or perthio-benzoato derivatives).

(II) *Mixed Nickel*(II) *Dithio- and Perthio-carboxylates,* (RCS$_2$)Ni(S$_3$CR). These are formed by stepwise desulphuration of (RCS$_3$)$_2$Ni, or by mixing equimolar amounts of (RCS$_3$)$_2$Ni and (RCS)$_2$Ni. They are more stable with aromatic substituents, and no compound of this type could be isolated, or is even formed, from dithioacetate or dithiophenylacetate, in solution. Among aliphatic dithiocarboxylates, only Ni(dtpv)(dtpvS) is formed in solution (but not isolated). Mixed dithiocarboxylate–perthio-carboxylates seem to form a more homogeneous group than the corresponding dithiocarboxylates.

They are monomeric, containing the square planar NiS$_4$ group, as demonstrated chemically by Fackler and Coucouvanis,[11] and proved by a structure determination for R = 4-propylphenyl.[29] The electronic spectra of the aromatic compounds (R = phenyl; tolyl) have a band (possibly *d–d*) *ca.* 13 kK (log ε *ca.* 2) which shows considerable shifts between solid state and solution, followed by a very characteristic high intensity band at 19 kK (3·9—4·0), with a shoulder just before 23 kK (log ε *ca.* 3·7). Internal ligand bands occur in the far-u.v. The aliphatic complex Ni(dtpv)(dtpvS) has a similar sequence of bands, except that all frequencies are shifted by some 2 kK to higher values.[3]

(III) *Bis*(*perthiocarboxylato*)*nickel*(II) *Complexes.*—Again this is a relatively homogeneous group, also more stable with aromatic perthiocarboxylato-ligands [apart from perthiopivalatonickel(II)]; they are monomeric,[3,21] having a square planar stereochemistry.

The electronic spectra have a ligand field band (log ε *ca.* 1·7) *ca.* 12 kK, an intense band *ca.* 18 kK (log ε *ca.* 3·5) with a characteristic shoulder *ca.* 16·0 kK (log ε *ca.* 2·7), followed by internal ligand bands in the u.v. Again, bands in the spectrum of the aliphatic compound are shifted *ca.* 2 kK to higher frequencies (apart from the *d–d* at *ca.* 12 kK) with respect to the aromatic compounds. Bis(perthiocarboxylato)nickel(II) complexes have been the subject of a separate paper[3] and their properties are reported here only for comparison. It is noted that the spectra of dithio-perthio-carboxylato-complexes are by no means an average or mixing of those of the analogous bis-dithio- and bis-perthio-carboxylato-complexes (at least in the visible and near u.v. regions). This indicates that extensive mixing of the electronic structures of the Ni^{2+} ion and of the chelating ligands occurs by individual mechanisms and cannot easily be described by any single choice of additive and/or transferable parameters referring only to the metal or ligand moieties, nor by any other factorization of electronic structure parameters.

Unlike the dithiocarboxylates, mixed dithioperthio- and bis-perthio-carboxylato-complexes do not easily form 1 : 2 pyridine adducts. The adducts are formed only in pure pyridine solution, in which their spectra are almost identical with those of the more stable bis-dithiocarboxylato-adducts, and still different from other [NiS$_4$N$_2$] chromophores in having high Δ_{av} values. The unique electronic structures of dithio- and perthio-carboxylatonickel(II) complexes are more evident in the [NiS$_4$] chromophores than in their pseudo-octahedral adducts. Although the latter do not correlate well with similar nickel(II) chromophores, they fit a ligand field model more closely, and show little detectable changes in spectra with change in substituents.

DISCUSSION

The data clearly show that although nickel(II) complexes with dithio- and perthio-carboxylato-ligands are based upon the common [NiS$_4$] chromophore, they display a wide variety of structural types. These include mono-, bi-, and tri-nuclear co-ordination, bridging, and chelating groups, four- and five-membered chelate rings, chelate $\widehat{\mathrm{SNiS}} \gtrsim 90°$ or $<90°$, and Ni–S distances *ca.* 2·16 or *ca.* 2·25 Å (the former structure occurring with perthiocarboxylate, and the latter with dithiocarboxylate ligands). Significant changes in electronic spectra accompany all these structural changes. Some simple speculations have been suggested,[3,30] and others will now be put forward in an attempt to rationalize the structural data.

The smaller Ni–S distance in the five-membered perthiocarboxylate rings resembles the situation in 1,2-dithiolato-complexes. This may be correlated with the alternation of signs of a.o.s in the π_v and π_v* m.o.s of the ligand moieties, which allows better net π_v-bonding effects in five-membered than in four-membered rings.[30] Furthermore, the larger bond angles at the co-ordinated sulphur atoms in the former type of ring provide better availability of in-plane lone pairs of sulphur for π_h*-antibonding with the nickel(II) orbitals. This may explain the lower in-plane ligand field strength and lower $\bar{\nu}(d–d)$ transition frequencies observed.[3]

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Extension of such qualitative and partial explanations requires care. Any attempt at a rationalization of such unique structural facts must parallel rationalization of the equally unique, perhaps even peculiar, electronic structures of the complexes.

The electronic spectra of dithio- and perthio-carboxylato-nickel(II) complexes are very different from those containing other chelating anionic sulphur ligands such as dtc, ept, or xant; the many intense low-energy transitions suggest similarity to $Ni(mnt)_2^{n-}$ complexes, but it is difficult to justify this with the dithiocarboxylates (which are 1,1-dithiolates). It is even more difficult to justify the presence of conjugation effects through the disulphide linkage in the perthiocarboxylates comparable to those along the π-conjugated skeleton of mnt^{2-}. Furthermore, this analogy with mnt^{2-} is incapable of accounting for the pronounced differences between differently substituted dithiocarboxylates. Thus a satisfactory explanation will require a new theoretical treatment specific to dithio- and perthiocarboxylato complexes of nickel(II).

The general picture, however, is one of more efficient mixing of ligand and nickel valence orbitals than occurs in any other nickel(II) complex. Consequently, a simple localization of valence orbitals as ligand field, charge transfer, or internal-ligand is no longer possible. In this respect the spectral changes occurring in the mixed dithio–perthio-carboxylato-complexes are particularly significant. On going from conjugated aromatic to aliphatic organic groups in the ligand, the *whole* spectrum (' ligand field ' bands in the visible region included) shifts some **2—3** kK to the blue. Thus, a structural change in the ligand affects all excited states (or at least, all those spectroscopically accessible) in nearly the same manner. Why is there such strong intermixing of valence orbitals in these complexes and not in those with dtc, ept, and xant? An obvious observation is that the former contain only virtually neutral carbon atoms (or sulphur of disulphide bridges), apart from the donor S atoms, and lack the electronegative substituents of the latter ligands (N in dtc, O in xant, P in ept). This may result in higher ligand orbital energies, hence better matching and more profound mixing with metal orbitals. This is only a qualitative speculation, of course, and will be substantiated only by complete MO calculations. Furthermore experimental evidence will be gained from investigation of nickel(II) complexes with dithiocarboxylates containing strongly negative substituent groups. Synthetic work in this direction is now in progress.

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