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Infrared Spectral Studies of Dithio- and Perthio-Carboxylato Complexes

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Chimica. — *Infrared Spectral Studies of Dithio- and Perthio-Carboxylato Complexes* (*). Nota di OLIVO PIOVESANA, CLAUDIO FURLANI, ALBERTO FLAMINI, ANTONIO SGAMELLOTTI e CARLO BELLITTO, (*) presentata (**) dal Corrisp. G. SARTORI.

RIASSUNTO. — Sono state studiate le proprietà vibrazionali di una serie di complessi di Ni(II) e Zn(II) con leganti ditio- e pertiocarbossilici. Le vibrazioni discusse sono quelle localizzate sui gruppi $—CS_2^-$, $—CS_2S^-$, Ph—C e S—S. Le frequenze relative variano con il carattere aromatico o alifatico del legante, con la presenza di un anello chelato a 4 o 5 termini, etc.; riflettendo differenze già note nella struttura elettronica e nella stereochimica.

INTRODUCTION

There has been much interest in 1,1–dithiolate complexes of transition metal ions, as witnessed by the recent proliferation of review articles on the chemical and structural properties of these compounds [1–4].

Virtually all 1,1–dithiolate ligands form complexes with Ni(II). These have a common behaviour in being diamagnetic, completely chelated species, containing an approximately square planar [NiS_4] chromophore. However, the nature of the substituent linked to the chelating groups has a marked influence on the electronic and stereochemical properties of the Ni(II) 1,1–dithiolates [5]. Particularly, dithio- and perthiocarboxylato complexes display a wide variety of structural and spectroscopic types, which, on the whole, are different from those of complexes containing other chelating anionic sulphur ligands, such as dithiocarbamate (dtc^-), xanthate ($xant^-$), phosphorodithioate (ept^-). An attempt to correlate the electronic and structural properties of dithio- and perthiocarboxylato complexes of Ni(II) has recently been made [5].

The vibrational behaviour of transition metals dtc^- and $xant^-$ complexes has received considerable attention [1] and, e.g., i.r. data are currently used to evaluate the extent to which the various resonance forms of the ligands in the complexes contribute to the structure [6].

Much less vibrational information is available in the case of dithio- and perthiocarboxylato complexes. We present the results of an i.r. investigation performed on a wide series of Ni(II) bis-dithio, dithio-perthio and bis-perthio carboxylates, some of the parent ligands and some of the analogous Zn(II) complexes. Vibrational data on vanadium(IV) tetrakis dithiocarboxylates and some preliminary assignments of selected frequencies of Ni(II)

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dithiocarboxylato complexes have been presented previously by one of us [7]. The vibrations of main interest are those localised on the $—CS_2^-$, $—CS_2S^-$, Ph—C and S—S groups, since the assignment of these modes might point out differences from dtc^- or $xant^-$ complexes, between aliphatic and aromatic complexes, four or five membered rings etc.

Our results and assignments on aromatic dithiocomplexes are corroborated by those obtained in a parallel, more detailed analysis of dithiobenzoato complexes of several metal ions [8].

Results and discussion

Tables I and II report infrared frequencies of the investigated compounds (1) in the 1400–400 cm^{-1} region. The bands due to the aliphatic or aromatic substituents either remain unchanged or are shifted slightly when the free ligands are converted into their metal complexes. They have been assigned by fingerprint technique and will not be discussed here. The assignment of the stretching frequencies of the chelating rings have been made by comparison with the spectral bands of dithioesters, dithioacids and alkali metal dithiocarboxylates. There is agreement that, in dithio-, thiono- and thiolo-esters $\bar{\nu}$ (C=S) and $\bar{\nu}$ (C—S) lie at ca. 1220 and 670 cm^{-1}, respectively [9]. These frequencies are little affected by the nature of the substituent R in R—CSSR′; e.g. $\bar{\nu}$ (C=S): 1225, dtaR′; 1226 dtbR′; 1215, dtpaR′; $\bar{\nu}$ (C—S): 668, dtaR′; 667, dtbR′; 663, dtpaR′ (R′ = carboxymethyl group) [10, 11]. On going from dithioesters to the corresponding dithioacids, $\bar{\nu}$ (C=S) is shifted to lower and $\bar{\nu}$ (C—S) to higher energy. This energy shifts are markedly dependent on the substituent linked to the CSS group. Thus, $\bar{\nu}$ (C=S) and $\bar{\nu}$ (C—S) are at 1124, 1097 and 778 cm^{-1} in dtpvH; 1216, 1192 and 581 cm^{-1} in dtaH; 1065 and 841 cm^{-1} in dtbH.

On complex formation, $\bar{\nu}_{as}$ (CSS) and $\bar{\nu}_s$ (CSS) of the chelated rings are found at lower and higher frequencies than those of $\bar{\nu}$ (C=S) and $\bar{\nu}$ (C—S) of the free acids. The energy separation between $\bar{\nu}_{as}$ and $\bar{\nu}_s$ (CSS) is markedly smaller in dithioaromatic than it is in dithioaliphatic complexes ($Ni(dtb)_2$: $\bar{\nu}_{as}$ (CSS) = 980 cm^{-1}, $\bar{\nu}_s$ (CSS) = 945 cm^{-1}; $Ni(dta)_2$: $\bar{\nu}_{as}$ (CSS) = 1173, 1147 cm^{-1}, $\bar{\nu}_s$ (CSS) = 899, 978 cm^{-1}). Zinc(II) and vanadium(IV) dithiocarboxylates show approximately the same frequencies [7]. This indicates that the CS_2 modes are rather insensitive to the geometry around the metal.

The phenyl-carbon stretching vibration in dtbH is identified in a strong band at 1250 cm^{-1}, shifted to 1266 cm^{-1} in $Ni(dtb)_2$, 1276 cm^{-1} in Ni(dtb)(dtbS) and 1253 cm^{-1} in $Ni(dtbS)_2$. Similar frequencies are found in nickel(II) complexes with dtt^- as a ligand. In contrast to ref. 12, we believe that these bands cannot be reasonably assigned to $\bar{\nu}$ (C=S) or $\bar{\nu}_{as}$ (CSS), since delocalisa-

(1) Abbreviations used in text: CH_3CSS^-, dta^-; $(CH_3)_3CCSS^-$, $dtpv^-$; $C_6H_5CH_2CSS^-$, $dtpa^-$; $C_6H_5CSS^-$, dtb^-; $p\text{-}CH_3C_6H_4CSS^-$, dtt^-.

TABLE I

Infrared spectra (cm^{-1}) of aliphatic dithio- and perthiocarboxylates between 400 and 1400 cm^{-1} (nujol mulls).

*dta*H [a]	Ni(*dta*)$_2$	*dtpv*H	Ni(*dtpv*)$_2$	Ni(*dtpv*S)$_2$	Zn(*dtpv*S)$_2$	ASSIGNMENT
450 *m*	438 *w*	450 *vw*	440 *vw*	440 *vw*	440 *vw*	Δ
458 *sh* 510 *vw*	520 *vw*					
				520 *s*	525 *s*	$\bar{\nu}$ (S—S)
	590 *w*	550 *vw* 593	580 *vw*	570 *w*	568 *w*	
581 *s*		772 *s*				$\bar{\nu}$ (C—S)
663 *vw* 691 *vw*		695 *vw*	652 *vw*			
726 *w* 745 *w*	720 *w*	730 *w* 760 *w*	710 *w*	728 *w*	715 *w* 793 *vw*	comb.
860 *s*		857 *s*				δ (S—H)
873 *sh*		865 *vw* 893 *vw*		810 *w*		
903 *m*	950 *w*	938 *s*	942 *m*	940 *w*	951 *m*	$\bar{\nu}$ (C—C)
	878 *s* 899 *s*		953 *s*	1000 *s*	982 *s*	$\bar{\nu}_s$ (CSS)
989 *w* 1010 *vw*	1010 *w*	1005 *sh*	1000 *sh*	1010 *sh*		comb.
1037 *vw*		1030 *m*	1030 *s*	1030 *w*	1020 *sh*	
			1048 *s*	1082 *s*	1060 *vs*	$\bar{\nu}_{as}$ (CSS)
1072 *m*	1080 *sh*	1070 *sh*				
1107 *s*	1100 *m*					ρ (CH_3)
		1152 *w*	1160 *w*	1160 *vw*	1150 *vw*	
1192 *s* 1216 *s*	1147 *s* 1173 *s*	1097 *w* 1124 *s*				$\bar{\nu}_{as}$ (CSS) or $\bar{\nu}$ (C=S)
		1220 *w* 1290 *sh*	1210 *w* 1250 *w*	1220 *m* 1240 *m*	1217 *m*	
1281 *vw*	1270 *vw*	1260 *sh*				
1357 *s*	1357 *s*	1368 *s*	1360 *s*	1372 *s*	1360 *s*	δ (CH_3)

(*a*) Previous measurements in ref. (17).

TABLE II. — *Infrared spectra* (cm^{-1}) *of aromatic and arylaliphati*

*dtpa*H	$Ni_2(dtpa)_4$	*dtb*H	Na*dtb*	Ni(*dtb*)$_2$	Ni(*dtb*) (*dtb*S)	Ni(*dtb*S)$_2$
	450 *w* 470 *w*	440 *vw* 470 *vw*	430 *w* 450 *w*	434 *w*	430 *w* 460 *w*	440 *w, bv*
					520 *m* 540 *w*	520 *m* 543 *m*
580 *w*	582 *w*	580 *w*	561 *w*	561 *w* 568 *w*	560 *w*	
628 *w*	619 *vw*	618 *w*	625 *vw*	613 *w*	652 *w*	620 *w*
640 *w* 670 *sh* (*a*)	655 *ms*	653 *m*	660 *mw*	666 *m*	666 *sh*	660 *w*
703 *vs* 758 *s*	697 *vs* 754 *s*	690 *s* 767 *s*	690 *s* 765 *s*	675 *s* 761 *s*	672 *s* 752 *s*	687 *s* 745 *s*
810 *w*	800 *vw* 846 *vw sh*	800 *vw*	840 *sh*	840 *vw* 843 *w*	825 *vw*	850 *sh*
860 *m* 875 *m*	853 *mw* 865 *s*	841 *ms* (*a*) 885 *w*	858 *mw* 875 *mw*			
903 *w* (*b*) 915 *w*	912 *vw*	940 *sh*		920 *w*	915 *vw*	925 *w*
		945 *ms* (*c*)	912 *m* 925 *sh*	945 *m*	909 *w* 952 *w*	918 *vw*
975 *w*	970 *vw*		975 *sh*	961 *sh*		970 *w*
	1019 *m* (?)		1018 *s*	980 *s*	986 *s* 1025 *s*	1030 *s* 1037 *vs*
1003 *w*	1003 *w*	1010 *w*	995 *w*	1000 *w*	999 *w*	1000 *w*
1033 *vs* (*d*)	1026 *sh* 1031 *s* (*d*)	1038 *w*	1040 *sh*	1028 *vw*		
	1041 *vs* (*e*) 1068 *w*	1065 *vs* (*f*)	1070 *sh*	1066 *vw*		
1088 *vs* (*d*)	1081 *ms* (*d*)	1091 *w*	1090 *w*		1096 *vw*	1080 *vw*
1130 *m* 1152 *m*	1158 *w*	1120 *mw* 1168 *vw*	1115 *w* 1170 *vw*	1158 *w*		1150 *sh*
1165 *sh* 1195 *m*	1186 *w*	1192 *m*	1190 *mw*	1182 *m*	1179 *m* 1188 *vw*	1190 *m*
	1212 *w*	1220 *sh*	1205 *vw*	1210 *sh* 1229 *sh*	1239 *w* 1247 *vw*	1235 *sh*
1235 *m*	1225 *ms*	1250 *vs*	1230 *s*	1266 *vs*	1276 *vs*	1253 *s*
1225 *m* (*f*) 1290 *w*	1290 *vw*	1270 *sh*				
1335 *w*	1324 *vw* 1337 *w*	1320 *w* 1350 *w*	1320 *w* 1350 *sh*	1318 *w*	1309 *w* 1331 *m*	1320 *w*

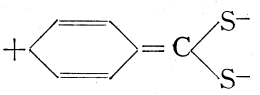
Φ = phenyl ring; ω_x = substituent-sensitive phenyl vibration; (*a*) $\bar{\nu}$ (C — S); (*b*) $\bar{\nu}$ (H_2C—CSS);

dithio- and perthiocarboxylates between 400 and 1400 cm^{-1} (nujol mulls).

Zn(*dtb*S)$_2$	Ni(*dtt*)$_2$	Ni(*dtt*)(*dtt*S)	Ni(*dtt*S)$_2$	Zn(*dtt*S)$_2$	ASSIGNMENT
420 *vw* 440 *vw*	443 *w*	440 *w*	420 *w* 440 *w*	430 *w* 450 *w*	π (phenyl ring)
532 *s* 542 *sh*		520 *w* 535 *w*	510 *m* 540 *m*	528 *s* 548 *w*	$\bar{\nu}$ (S—S)
	590 *w*	555 *w* 590 *w*	590 *w*	583 *w*	Φ and CH_3
605 *w*	630 *w*	630 *w*	630 *w*	630 *w*	α (C—C—C)
645 *w*		660			δ (CSS)
672 *s* 740 *s*	788 *m* 810 *s*	790 *sh* 805 *vs*–810 *sh*	780 *w* 810	780 *w* 810 *s*	monosubstd. Φ,π (C–H) (col. 1-8) disubstd. Φ, C–H out of plane (col. 9-12)
840 *sh*	838 *sh*	860 *sh*	845 *vw*	850 *sh*	χ (C—H)
					C—H out of plane (?)
					not assigned
892 *w*	948 *s*	925 *sh* 955 *w*	930 *sh*	900 *vw* (?)	$\bar{\nu}_s$ (CSS)
960 *w*			970 *w*	970 *w*	
1013 *s* 1025 *sh*	972 *s*	972 *m* 1030 *vs*	1033 *vs*	1018 *vs*	$\bar{\nu}_{as}$ (CSS)
995 *w*	1000 *sh* 1008 *mw*	1010 *sh*	1010 *sh*		ring breathing
					ρ (C—H)
			1040 *sh*	1060 *vw*	
1070 *w*		1085 *m*			ρ (C—H)
1140 *sh*	1130 *w*	1125 *sh*	1150 *sh*	1130 *vw*	
1180 *m*	1177 *vs*	1182 *s*	1182 *vs*	1180 *vs*	ρ (C—H) and in plane Φ
1210 *sh* 1220 *sh*	1220 *sh*		1210 *w*	1210 *w*	ω_x
1238 *s*	1272 *vs*	1290 *vs*	1243 *vs*	1223 *vs*	$\bar{\nu}$ (Φ—C)
	1287 *sh*			1270 *sh*	
1325 *w*	1315 *w*	1310 *w*	1310 *w*	1310 *w*	$\bar{\nu}$ (C—C) phenyl
	1370 *s*	1365 *ms*	1370 *s*	1370 *s*	δ (CH_3)

(*c*) δ (S—H); (*d*) $\bar{\nu}$ (CH_2); (*e*) possibly $\bar{\nu}_{as}$ (CSS); (*f*) $\bar{\nu}$ (C = S).

tion of negative charge should decrease, rather than increase, these frequencies ($\bar{\nu}$ (C=S) in dtbR′ is at 1226 cm^{-1}, in dttR′ at 1225 cm^{-1}). Bands at 1210–1230 cm^{-1} have been assigned to $\bar{\nu}$ (Ph—C) in some monothiobenzoato metal complexes [13]. For aromatic dithiocarboxylato complexes, rather high $\bar{\nu}$ (Ph—C) frequencies, small differences between $\bar{\nu}_{as}$ and $\bar{\nu}_{s}$ (CSS) and relatively low energy as compared with those of the aliphatic analogous, suggest that polar resonance forms such as:



may be important. These forms may be correlated with the planarity of the Ph—CSS group and the rather short Ph—C bond distance, as shown by X-ray analysis of $Ni(dtb)_2$ [14]. In $Ni_2(dtpa)_4$, the many fingerprint frequencies in the same region and possible interactions between bridging ligands [15] make the identification of the CS_2 frequencies uncertain.

Aromatic bis-perthiocomplexes, as compared with the corresponding dithioanalogous, clearly show $\bar{\nu}$ (Ph—C) at lower, and $\bar{\nu}_{as}$ (CSS) at higher frequencies. $\bar{\nu}_{s}$ (CSS) is located at ca. 920 cm^{-1}, i.e. at lower frequencies. This assignment is tentative due to the weakness of the bands and to the occurrence of several absorptions in this spectral region. The assignments above are consistent with a decrease in conjugation effects from dithio to perthiocomplexes. Aliphatic bis-perthiocarboxylates show a different behaviour since in $Ni(dtpvS)_2$ both the antisymmetric and symmetric carbon-sulphur stretching modes appear as strong absorptions and at higher frequencies than in $Ni(dtpv)_2$. The spectral behaviour of mixed dithio-perthiocarboxylatocomplexes is expected to be complicated by the presence of four- and five-membered rings in the same molecule. If there were no coupling between the stretching vibrations of the two different chelated rings, two bands due to $\bar{\nu}$ (Ph—C) and four bands due to the carbon-sulphur vibrations (two for each ring) might be expected. In Ni(dtb) (dtbS) and Ni(dtt) (dttS) only one band attributable to $\bar{\nu}$ (Ph—C) is observed (at 1276 and 1290 cm^{-1}, respectively) and at higher energy than in the corresponding bis-dithio- and bis-perthiocomplexes. In contrast, Ni(dtb) (dtbS) shows bands at 909, 952, 986 and 1025 cm^{-1}, i.e. frequencies very close to those of the CS_2 group in $Ni(dtb)_2$: 980 and 945 cm^{-1} and in $Ni(dtbS)_2$: 1073, 1030 and ca. 920 cm^{-1}. Similarly Ni(dtt) (dttS) shows bands at 925, 955, 972 and 1030 cm^{-1}; $Ni(dtt)_2$: 972 and 948 cm^{-1}; $Ni(dttS)_2$: 1030 and 930 cm^{-1}. A more accurate analysis is needed to explain why only one $\bar{\nu}$ (Ph—C) and four CSS vibrations are present in these mixed complexes.

$\bar{\nu}$ (S—S) vibrations (often doublets) are found in the region 520–550 cm^{-1}. ν (M—S) frequencies probably occur below 400 cm^{-1} and were not observed here. On the whole, the spectral behaviour of dithiocarboxylato complexes is markedly different from that of other dithio-complexes (e.g. dithiocarbamates and xanthates) containing the CSS group.

The i.r. data are insufficient to be able to decide how differences in resonance or inductive effects, bridging ligands etc., may be important in determining the observed spectral patterns. It may be noted, however, that differences in the electronic spectra and bonding between dithiocarboxylates and other dithiocomplexes such as dithiocarbamates or xanthates and even between aliphatic and aromatic dithiocarboxylates are reflected by differences in their i.r. spectra.

EXPERIMENTAL

All the compounds were prepared according to ref. [5]. The i.r. spectra were measured by Beckmann IR 10 and, or, Perkin Elmer 521 spectrophotometers.

Note. In the course of our preparation of this manuscript, a paper by J.M. Burke and J. P. Fackler Jr. appeared [16] which reports vibrational data on complexes of Ni(II), Pd(II) and Pt(II) with dithio- and perthio aromatic ligands. The assignments which have been made by these authors are in substantial agreement with ours.

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