Infrared Investigation on Aromatic and Aliphatic Dithio-acids as Ligands. Part 2.† The Infrared Spectra of Bis(trithioperoxybenzoato)-zinc(II) (Polarised) and -nickel(II)

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Infrared band assignments for bis(trithioperoxybenzoato)zinc(II) [Zn(S$_3$CPh)$_2$], are reported, based on polarisation measurements on polycrystalline iso-orientated samples. The results confirm most of the assignments previously proposed for dithiobenzoatometal complexes and strongly support the assignment of ν(S–S) to a weak absorption at 655 cm^{-1}. The spectral comparison with the corresponding nickel compound and analogous compounds is discussed.

WE report the results of i.r. experiments on orientated crystal layers of bis(trithioperoxybenzoato)zinc(II), obtained with the intention of refining the understanding of its spectrum and of previous vibrational assignments for dithio- and perthio-carboxylato-complexes.[1-12]

EXPERIMENTAL

The title compounds were prepared and purified following the procedure of Flamini *et al.*[4] Their thermal stability was first checked by spectral comparison of samples obtained by random crystallisation from melts and the corresponding Nujol mull or KBr disc. The compound [Ni(S$_3$CPh)$_2$] undergoes decomposition under fusion, while [Zn(S$_3$CPh)$_2$] gives reproducible spectra, even after several annealings.

Orientated polycrystalline layers of [Zn(S$_3$CPh)$_2$] were obtained by slow crystallisation of the melt across a temperature gradient. The normal habit from the melt was tabular on (10$\bar{1}$) and this allowed the spectrum to be observed with the E vector either along the b axis or along the [101] direction. Another type of orientated sample was obtained by aligning on a CsI window several well developed single crystals (obtained from solution), first mulled in Nujol or Fluorolube. Since this sample was thick, it was especially suitable for investigating the polarisation properties of weak bands. In Table 4 the absorptions observed with this second orientated sample are marked with an asterisk.

The polarised i.r. spectra were recorded between 4 000 and 400 cm^{-1} on a Beckmann IR-9 spectrophotometer and between 600 and 250 cm^{-1} on a Perkin-Elmer model 525 spectrograph, equipped with a wire-grid polariser. Spectra of the compounds as KBr pellets at liquid-nitrogen temperature were obtained between 4 000 and 400 cm^{-1} using a conventional low-temperature cell. Attempts to obtain Raman spectra failed, since the compounds decompose in the laser beam.

RESULTS AND DISCUSSION

Vibrational Analysis.—The compounds [Zn(S$_3$CPh)$_2$] and [Ni(S$_3$CPh)$_2$] crystallise in the monoclinic system, space groups $C2/c$ and $P2_1/c$ (C_{2h}^5), respectively.[13] The zinc compound has four molecules in the unit cell on sites of C_2 symmetry, whereas the nickel compound has two molecules per unit cell on sites of C_i symmetry. The number of vibrations for each symmetry class and the selection rules under the molecular or site group (free-molecule vibrations) and the factor group (unit-cell vibrations) are listed in Tables 1 and 2. As shown by the correlations in Table 1, the spectrum of the zinc compound can be correctly interpreted on the basis of the site-group analysis.

In [Zn(S$_3$CPh)$_2$], the 44 molecular normal modes of A symmetry (derived from in-phase couplings with respect to C_2 of equivalent deformations of half of the molecule) will be polarised along b, whilst the 43 normal modes of B symmetry (out-of-phase couplings) will be polarised in a direction perpendicular to b. Those of the latter modes having transition moments perpendicular to the (10$\bar{1}$) face should be absent or, at least, very weak in the polarised spectrum. The spectrum of the zinc compound should, therefore, consist of doublets of bands of A and B symmetry, respectively, their frequency separation being indicative of the degree of vibrational coupling of corresponding deformations of half of the molecule across the metal atom. Lack of band polarisation should be related to weak coupling of

TABLE 1

Correlation diagram and selection rules for [Zn(S$_3$CPh)$_2$]

C_2 (molecule and site)	C_{2h} (crystal)	I.r. activity
(44) A	A_u (44)	b
(43) B	B_u (43)	a, c

TABLE 2

Correlation diagram and selection rules for [Ni(S$_3$CPh)$_2$]

C_i (molecule and site)	C_{2h} (crystal)	I.r. activity
(45) A_u	A_u (45)	b
	B_u (45)	a, c

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† Part 1 is ref. 8*b*.

[1] E. Uhlig and E. Uebel, *Z. anorg. Chem.*, 1965, **337**, 98.

[2] J. P. Fackler, jun., D. Coucouvanis, J. A. Fetchin, and W. C. Seidel, *J. Amer. Chem. Soc.*, 1968, **90**, 2784.

[3] E. Lindner and U. Kunze, *Chem. Ber.*, 1969, **102**, 3347; E. Lindner and D. Langner, *Z. Naturforsch.*, 1969, **B24**, 1402; E. Lindner, R. Grimmer, and H. Weber, *J. Organometallic Chem.*, 1970, **23**, 209; E. Lindner and R. Grimmer, *ibid.*, **25**, 493.

[4] A. Flamini, C. Furlani, and O. Piovesana, *J. Inorg. Nuclear Chem.*, 1971, **33**, 1841.

[5] O. Piovesana and C. Furlani, *Chem. Comm.*, 1971, 256.

[6] O. Piovesana and G. Cappuccilli, *Inorg. Chem.*, 1972, **11**, 1543.

[7] T. M. Burke and J. P. Fackler, jun., *Inorg. Chem.*, 1972, **11**, 3000.

[8] (*a*) M. Maltese, *Proc. 13th Internat. Conf. Co-ordination Chem.*, Cracow–Zakopane, 1970, vol. 2, p. 116; (*b*) *J.C.S. Dalton*, 1972, 2664; (*c*) *Proc. Internat. Conf. Molecular Spectroscopy*, Wrocław, 1972, p. 88.

[9] R. Engler, G. Gattow, and M. Dräger, *Z. anorg. Chem.*, 1972, **388**, 229.

[10] O. Piovesana, C. Furlani, A. Flamini, A. Sgamellotti, and C. Bellitto, *Atti. Accad. naz. Lincei*, 1973, **54**, 763.

[11] A. Flamini, *J. Co-ordination Chem.*, 1975, **14**, 205.

[12] O. Piovesana and L. Sestili, *Inorg. Chem.*, 1974, **13**, 2745.

[13] M. Bonamico, G. Dessy, V. Fares, and L. Scaramuzza, *J. Chem. Soc.* (*A*), 1971, 3191.

vibrations with comparable components of the transition moment on the normalised crystal axes.

Since, in the group-frequency approximation, the transition moment associated with a particular molecular vibration can be easily identified with some direction in the molecule, we have listed in Table 3 the (squared) cosines with respect to a set of normalised crystal axes (*a*, *b*, and *c**) and [101] of the directions (schematically indicated in the first column) along which the most representative transition moments should oscillate (see below).

TABLE 3

Squared cosines of some directions in the [Zn($S_3CPh)_2$] molecule

Direction †	Direction cosines on *a*	*b*	*c* *	[101]
C(1)–C(2)	0.81	0.04	0.15	0.02
C(3)–C(7)	0.17	0.04	0.79	0.94
S(1)–S(2)	0.79	0.03	0.18	0.02
Perpendicular to the benzene ring	0.01	0.92	0.07	0.03

† For atom numbering see ref. 13 (Figure 4).

Spectra and Assignments.—Some details of the polarised i.r. spectrum of the (10$\bar{1}$) face of [Zn($S_3CPh)_2$] are shown in Table 4, and are compared with the spectrum of the nickel analogue.

Benzene-ring vibrations. The normal modes localised in the benzene rings can be related to the normal vibrations of a monosubstituted benzene,[14] C_6H_5X (C_{2v} symmetry). Of the planar normal modes of such a molecule, the A_1 vibrations have their transition moment aligned with the C–X bond, while the B_1 transition moments lie perpendicular to this bond. As the C(1)–C(2) and C(3)–C(7) direction cosines indicate (Table 3), it is then expected that both types of band should be strongly polarised perpendicular to *b* and that the A_1 vibrations should be drastically reduced in intensity on passing from randomly orientated samples to the iso-orientated ones investigated here. On the other hand, modes with transition moments perpendicular to the benzene ring should have parallel polarisation.

As indicated in Table 4, most benzene-ring absorptions show the expected polarisation. Failure to observe the predicted effects is presumably due to mechanical coupling between benzene and chelate-ring vibrations, which causes the transition moments of some planar benzene-ring vibrations to lie out of the benzene plane. (The angle between the benzene and the chelate ring is 40° in the zinc compound and 33° in the nickel compound.[13]) In fact, most of the bands showing anomalous polarisation lie at *ca.* 1 000 cm^{-1}, where the strong C–S stretchings are located (see below).

A marked reduction in intensity on passing from randomly orientated to iso-orientated crystal spectra is clearly observed for the absorption at 1 242 cm^{-1}, which is therefore related to the highest-frequency phenyl-carbon absorption. This band appears at a lower wavenumber than in metal dithiobenzoates [8b] (1 270 cm^{-1}) probably because of the reduced conjugation with the chelate ring.

C–S *stretchings*. The intense broad absorptions at 1 036 and 1 025 cm^{-1} in the spectrum of randomly orientated [Zn($S_3CPh)_2$] (see Table 4) can be ascribed to the dithiocarboxylate groups, on the basis of both position [10] and intensity. These two bands can arise, in principle, (*i*) one from intramolecular coupling of ν_{asym}-(CSS), the other of ν_{sym}(CSS), or (*ii*) from in-phase and out-of-phase couplings of ν_{asym}(CSS) alone. [In this case, ν_{sym}(CSS) should have a lower frequency, as proposed in some analogous instances: see ref. 8*b* and literature therein.] However, the presence of two corresponding absorptions in the spectrum of the nickel compound (where the inversion centre makes the in-phase couplings i.r.-inactive) seems to support the former coupling mechanism. Furthermore, the *A* and *B* components of opposite polarisation for each of these absorptions are quite evident in the polarised spectra (see Table 4), even when the broadness or overlap of these absorptions makes it difficult to recognise their polarisation behaviour.

The presence of both ν_{asym}(CSS) and ν_{sym}(CSS) at *ca.* 1 000 cm^{-1} in the present compounds definitely supports the assignments previously proposed for the analogous strong absorptions observed in this same range for other carboxylatometal complexes (dithiobenzoates [8b] and phenyldithioacetates [8c]). As the scarce evidence for *A* and *B* components indicates weak coupling across the Zn atom, the low-frequency separation between ν_{asym}(CSS) and ν_{sym}(CSS) should imply weak coupling even between C–S stretchings in the same chelate ring. This seems to be in conflict with the observed C–S bond distances which show a difference of 0.02 Å in the zinc compound and 0.01 Å in the nickel compound.[13] The fact that the C–S stretching frequencies in the present compounds are higher than in the corresponding dithiobenzoates [8b] is probably due to the reduced conjugation between the chelate rings and the benzene rings, even if the presence of the S–S bond in the chelate ring undoubtedly introduces further mechanical complication.

S–S *stretching*. The absorption associated with this vibration should, in principle, be weak, because of the low polarity of the S–S bond. Furthermore, since S–S bonds are perpendicular to the crystal face investigated here (see Table 3), marked decrease in intensity should be observed on passing from randomly to iso-orientated crystal spectra. These two requirements are met by the band at 655 cm^{-1}, which, therefore, is assigned to ν(S–S). This frequency seems to be higher than those normally found for this vibration in compounds containing disulphide linkages (430—550 cm^{-1} in organic disulphides [15-17]) and this assignment has been practically

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[14] See ref. 10 of ref. 8*b*.

[15] L. J. Bellamy, 'Infra-red Spectra of Complex Molecules,' Methuen, London, 1958, p. 352.

[16] K. Nakanishi, 'Infrared Absorption Spectroscopy,' Holden-Day, San Francisco, 1962, p. 54.

[17] N. B. Colthup, L. H. Daly, and S. E. Wiberley, 'Introduction to Infrared and Raman Spectroscopy,' Academic Press, New York, 1964, pp. 306, 344.

TABLE 4

Wavenumbers (cm^{-1}), polarisation, and assignments of the i.r.-active modes of [Zn(S$_3$CPh)$_2$] and [Ni(S$_3$CPh)$_2$]

	[Zn(S$_3$CPh)$_2$]			
[Ni(S$_3$CPh)$_2$] [a]	a	iso-orientated samples [b]	Polarisation (with respect to b) [c]	Assignment [d]
e	e	3 084 *	⊥	ω_1, ω_2, ω_3, ω_{15}, ω_{16}
		3 072 *	⊥	
		3 059 *	∥>⊥	
		(3 057) *	⊥	
		3 036 *	⊥	
		(3 027) *	⊥	
		3 022 *	⊥	
	1 585mw	1 585	∥	ω_4
	1 569vw	1 569	⊥	ω_{18}
		1 518 *	⊥	ω_5
1 475w	1 483w	1 482	n.p.	
1 444s	1 443s	1 445	⊥	ω_{19}
	1 391vw	1 391	⊥	
	1 386vw	1 386	⊥	
1 330w	1 332w	1 332	⊥	ω_{20}
1 312w	1 311w	1 312	⊥	ω_{17}
	1 297vw	1 297 *	∥	
	1 278vvw	1 275 *	⊥	
1 249m	1 242m	1 241 *	⊥	ω_6
1 230mw	1 227mw	1 228 *	n.p.	
1 183mw	1 184mw	1 183	∥	ω_7
		1 160 *	⊥	ω_{21}
		1 153 *	∥	
1 105w	1 104w	1 104	∥	ω_{22}
1 082w	1 079mw	1 081	⊥	ω_8
		1 078	∥	
1 035vs	1 036vs	1 035	⊥	ν(CSS)
		1 032	∥>⊥	
1 028ms	1 025vs	1 027	∥>⊥	
		1 024	∥	
1 000m	998m	999	∥>⊥	ω_9
990w	991w	991	∥	
965w	969w	968	⊥	ω_{12}
	955vw	954 *	⊥>∥	ω_{25}
		942 *	⊥>∥	
922w		910	∥>⊥	ω_{26}
912w	901m	901	∥>⊥	
837vw	834vw	834	⊥	ω_{10}
	826vw	825	∥	ω_{13}
754vs	752vs	752	∥	ω_{27}
686s	685vs	686	∥	ω_{28}
659mw	655w			ν(S–S)
615w	617w	619	∥	ω_{23}
		617	⊥	
546mw	558vs	557	∥>⊥	ω_{11}
525m	(550)	(549)	⊥>∥	chelate-ring def.
	547s	546	∥	
500vw	478w	478 *	⊥>∥	chelate-ring def.
455mw	455w	455 *	⊥	ω_{14}
	435w	435 *	∥	ω_{29}
418w	423vw	423	n.p.	
401vw	400vvw	400 *	∥	ν(M–S)
366mw	348w	348 *	⊥	
	(332)	(332) *	∥	
314w	304w	304 *	⊥	
	290vw	290 *	∥	
	(280)	(280) *	∥	

[a] In KBr disc or Nujol mull. [b] Bands marked with an asterisk were observed only in the thicker iso-orientated sample. [c] n.p. = Non-polarised. [d] Numbering according to E. W. Schmid, J. Brandmüller, and G. Nonnenmacher, *Z. Electrochem.*, 1960, **64**, 726. [e] Bands obscured by the strong scattering of the sample.

followed in all the i.r. investigations on sulphur-rich metal dithiolates.[2,4,7,10,18] However, the intensity and polarisation of the band at 655 cm^{-1} offer the most convincing arguments that this assignment is correct.

Chelate-ring deformations. The distinction between bands due to chelate-ring deformations and benzene-ring absorptions below 600 cm^{-1} is somewhat difficult. In principle, because of the large angle between the chelate ring and the *b* axis, they should be non-polarised, but, because of the aforementioned coupling between benzene- and chelate-ring vibrations, benzene vibrations, as well, can be non-polarised. However, mechanical coupling, stronger between chelate than between benzene rings, should give rise to a more marked band splitting in the case of chelate-ring deformations. The bands at 558 and 547 cm^{-1} of [Zn(S$_3$CPh)$_2$] are both non-polarised,

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[18] D. Coucouvanis and J. P. Fackler, jun., *J. Amer. Chem. Soc.*, 1967, **89**, 1346.

but only the latter band shows distinct components of different polarisation. Furthermore, the spectra of metal dithiobenzoates exhibit weak absorptions at *ca.* 560 cm^{-1} which disappear under benzene-ring deuteriation,[8b] providing convincing evidence that the band at 558 cm^{-1} should be assigned to a benzene-ring absorption. The assignment of the band at 478 cm^{-1} to another chelate-ring deformation is based on similar arguments.

M–S *stretchings*. The metal–sulphur stretchings definitely lie below 400 cm^{-1}.[8b] In this range, the zinc compound shows two weak absorptions (at 348 and 304 cm^{-1}) with perpendicular polarisation, together with three other very weak parallel bands (a definite peak at 290 cm^{-1} and two shoulders centred at 332 and 280 cm^{-1}). The perpendicular bands are reasonably due to vibrations roughly described as out-of-phase couplings of the symmetric and antisymmetric stretchings of the ZnSS moiety. The two in-phase couplings have to be found among the remaining three parallel bands. In the case of the nickel compound, only two absorptions are expected and these are, indeed, found at 366 and 314 cm^{-1}.

The metal–sulphur stretching frequencies found in this work agree with those observed in metal dithiobenzoates.[8b] Nickel–sulphur stretchings appear at higher wavenumbers than the corresponding absorptions of the zinc compound, as expected on the basis of bond-strength considerations.

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