Complexes with Sulphur and Selenium Donor Ligands. Part III.† The Electronic Spectrum of Bis(dimethyl phosphorodithioato)-2,9-dimethylphenanthrolinenickel(II)

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The crystal polarised electronic spectrum of the title compound has been recorded at room temperature and at liquid-helium temperature in three orthogonal directions. From the observed polarisations of the absorption bands, a ground state $^3B_2$ has been deduced in an effective symmetry C_{2v}. This inversion in ground state from that previously found for trigonal bipyramidal C_{2v} symmetry is ascribed to the very large (*z*-axis) SNiN angles, *i.e.* the small ' bite ' angle of the phenanthroline ligand.

From a total of eleven bands observed at 4·2 K, three are assigned to spin-forbidden transitions, and the energy order, $^3B_1(^3E'') < {}^3A_2(^3E'') < {}^3B_1(^3A_2'') < {}^3A_2(^3A_1) < {}^3B_2(^3A_2') < {}^3B_1(^3E'') < {}^3B_2(^3A_2') < {}^3A_2(^3E'')$, suggested for the other eight (parent D_{3h} terms in parentheses). The transition within the split level $^3E'$ (D_{3h}) could not be located.

The energies of the bands in solid-state electronic spectra are similar to those in acetone solution, indicating predominant existence of the same five-co-ordinate species in solution.

THE electronic structures of five-co-ordinate nickel(II) complexes have been of interest for some time[1] and factors affecting high and low spin character[2] investigated and various crystal-field calculations performed.[3] Little work has as yet been reported on more accurate assignments and correlation of energy-level orders with molecular and electronic structure. Assignments have recently been put forward for $[NiN_5]$ (D_{3h})[4] and $[NiO_2N_3]$ (square based pyramidal, C_s effective symmetry)[5] chromophores on the basis of room-temperature polarised-crystal spectra. Not all the expected ' *d–d* ' bands were experimentally observed so full analyses were not possible. Although an apparently successful assignment of a $[NiO_5]$ (C_{4v}) chromophore has been reported,[6] a subsequent analysis of the polarised spectra of a $[NiN_4Br]$ (accurately C_{4v}) chromophore gave an assignment with relatively high intensity bands ascribed to $^1E \leftarrow {}^3B_1$ transitions. The breakdown of the normal spin-selection rules was ascribed to the high spin–orbit coupling constant of the bromide ion in the axial position.[7] It would seem that more single-crystal spectral work is necessary before firm conclusions can be drawn about electronic structure.

Because of this we have examined the electronic spectrum of $Ni[S_2P(OMe)_2]_2$,2,9-dimethylphenanthroline, using single-crystal methods. This complex is interesting for several reasons. First, it is high spin, despite the presence of three sulphur atoms co-ordinated to the nickel(II) ion and, secondly, the possible presence of π-bonding between S and Ni might give rise to significant differences in electronic energy level order compared with the case for only σ-bonding. In addition, the co-ordination lies between trigonal bipyramidal and square based pyramidal, and detailed electronic spectral data may give insight into the ambiguous and novel bonding situation present, as has previously been found in a distorted five-co-ordinate copper(II) complex.[9]

EXPERIMENTAL

Bis(dimethyl phosphorodithioato)nickel(II) was prepared by the standard procedure of allowing nickel chloride hexahydrate to react with an excess of P_2S_5–MeOH under a nitrogen atmosphere; the product was purified by recrystallisation from acetone. Large crystals of the adduct with 2,9-dimethylphenanthroline were obtained by slow crystallisation from ethanol–acetone.

The complex crystallises in space group $P2_1/c$, with $\beta = 92{\cdot}5°$, $a = 7{\cdot}86$, $b = 14{\cdot}51$, and $c = 21{\cdot}79$ Å, and crystals were obtained as flat plates developed on (001) and elongated along (100), with the end face (100) also developed. Spectra were recorded of thin sections of the (001) face and also of the (100) face after this had first been ground down carefully with acetone. This latter spectrum is expected to be a little less reliable than the others, but was probably well within ±5° of the *c'* spectrum, as shown by the coincidence of the *b* spectra for the two faces. The spectra were recorded at room and liquid-helium temperature on a Spex spectrometer equipped with optical system, high-pressure lamp, liquid-helium circuit, and temperature-monitoring device described previously.[10] Accurate baselines were recorded since only a single polariser was used. Room temperature spectra run on a Shimadzu MPS 50L spectrophotometer were used as a check and found to be identical. Since crystal sections were mounted in direct contact with the copper ' tongue ' of the cryostat *via* clean silver paste, the real temperature might be expected to be very close to the nominal one (4·2 K). A limitation of both these instruments is that spectra below *ca.* 10·5 kK (1 kK = 1000 cm^{-1}) cannot be obtained. These were recorded, on much

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† Part II, A. A. G. Tomlinson, *J. Chem. Soc.* (*A*), 1971, 1409.

[1] L. Sacconi, *Transition Metal Chemistry*, 1968, vol. 4, p. 199. Marcel Dekker Inc., New York; J. S. Wood, *Progr. Inorg. Chem.*, 1972, **16**, 277.

[2] L. Sacconi, *Co-ordination Chem. Rev.*, 1972, **8**, 351.

[3] M. Ciampolini and I. Bertini, *J. Chem. Soc.*, 1968, 2241; C. Furlani, *Co-ordination Chem. Rev.*, 1968, **3**, 141; J. R. Angus, G. M. Woltermann, and J. R. Wasson, *J. Inorg. Nuclear Chem.*, 1971, **33**, 3967.

[4] I. Bertini, M. Ciampolini, P. Dapporto, and D. Gatteschi, *Inorg. Chem.*, 1972, **11**, 2254.

[5] I. Bertini and D. Gatteschi, *J. Co-ordination Chem.*, 1971, **1**, 285.

[6] M. Gerloch, J. Kohl, J. Lewis, and W. Urland, *J. Chem. Soc.* (*A*), 1970, 3269.

[7] M. A. Hitchman, *Inorg. Chem.*, 1972, **11**, 2387.

larger sections but only at room temperature, on a Beckmann DK 1A instrument equipped with balanced nicol polarisers.

Structure attributable to interference effects (present both at room and low temperature) appeared around the 19·8 kK residual parallel to *a*, which allowed a thickness $d = 3{\cdot}9 \times 10^{-3}$ cm to be deduced.

Low-temperature spectra of thicker crystals did not show the presence of any further bands than those below.

Crystal axes were identified using *X*-ray oscillation and Weissenberg photographs.

Description of Crystal Structure and Results.—As seen from Figure 1, the crystal structure [8] of the complex shows it may be described in several different ways: (i) a distorted tetragonal pyramid with apex at N(2), (ii) a distorted trigonal bipyramid with N(2) and S(1) apical and, (iii) a distorted trigonal bipyramid with S(2) and S(3) ' apical '. In favour of the last description are the significantly longer Ni–S bond lengths for the two apical sulphur atoms and the very large S(1)NiN angles. The molecules are not accurately aligned in the unit cell but if the molecular axes of Figure 1 are assumed it is seen that the *z* axes of the molecules are almost completely aligned along the *b* axis (>99% *z*), *x* almost aligned along *c* (an axis orthogonal to *a* and *b*) (>80% *x*), and *a* contains a large amount of *y* character (*ca.* 75%). Figure 2 shows the alignment present *via* a projection on (001).

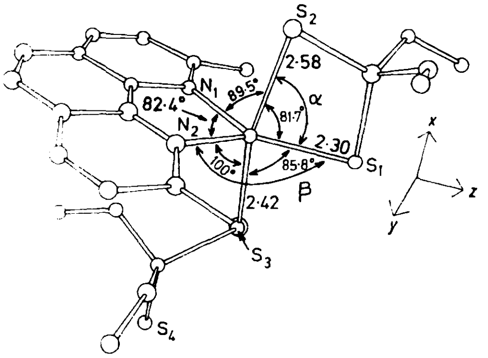

FIGURE 1 Molecular geometry of $Ni(mpt)_2(Me_2phen)$, with choice of axes assuming an approximately C_{2v} symmetry

Direction cosines (squared) referred to orthogonalised cell *a b c'*

	a	*b*	*c*
$\cos^2 z$ (Ni–S_1)	0·003	0·994	0·003
$\cos^2 x$	0·138	0·005	0·856
$\cos^2 y$	0·892	0·001	0·107
{$\cos^2$ (Ni–S_2)	0·142	0·005	0·853}
{$\cos^2$ (Ni–S_3)	0·224	0·022	0·752}

Both room- and low-temperature spectra are shown in Figure 3. At room temperature there are in all six absorption bands between 6 and 24 kK, with marked ' tails ' at *ca.* 20·0 kK parallel to *b* and at *ca.* 24 kK parallel to *a*. The band at *ca.* 14·6 kK is particularly broad. The greatest polarisation effects are found on the bands at 23·1, 14·4, and 11·6 kK, the first two being more intense parallel to *b* and the last parallel to *c'*. There is also a seventh ' band ' at 25 kK parallel to *a* and 26 kK parallel to *b*.

The spectra are considerably more clear at 4·2 K. Further bands appear at 15·4, 15·9, and 19·8 kK parallel to *c'* and a shoulder at *ca.* 21·5 kK present both parallel to *a* and parallel to *b*. The ' band ' at 25—26 kK moves to much higher energy than the others (*ca.* 0·8 kK) and also narrows considerably, which suggests that it might be an absorption edge, possibly containing a charge-transfer band, although this was not investigated further. This movement to higher energy disclosed the presence of yet another band at 23·8 kK parallel to *a*. The intensities of the bands at 11·8, 14·4, and 23·1 kK increase slightly at lower temperature, the band maxima remaining at the same energy, whilst those of the other bands decrease (although the behaviour with temperature of the band at 23·8 kK is rather difficult to establish). The total number of bands observed is eleven.

Assignment and Discussion.—The choice of an effective symmetry point group for the molecule appears to be relatively straightforward. Thus, all choices not having the unique axis between the nitrogen atoms may be ignored since, if S $\not\equiv$ N, electronically, which seems without doubt, they would all lead to a C_1 symmetry, which is obviously not the case given the polarisation effects. This leaves only C_{2v} or a subgroup. Since both C_2 and C_s predict qualitative coincidence in spectra between *x* and *y*, both may be ignored as effective point groups the spectra in these two directions are clearly different, a point made especially clear by the liquid-helium results. The most reasonable effective symmetry possible then seems to be C_{2v}.

There now arises the possibility that this effective symmetry is derived, not from D_{3h} symmetry but from C_{4v}, with a change of principal axis (although this appears unlikely considering the N_1NiN_2 angle of 82·4°). This may be discounted by noting that such a situation would give rise to selection rules predicting the absence of spin-allowed, electronically allowed transitions in the *z* direction (Table 1). This is clearly not in agreement with the spectrum of the complex in this direction (Figure 3).

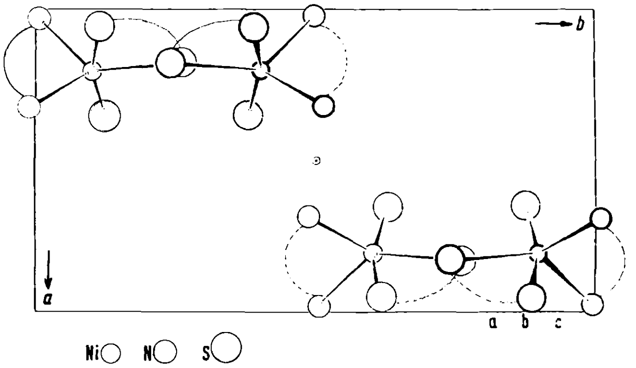

FIGURE 2 Projection of unit cell on (001) face (inset shows projections of unit vectors along NiS_1, NiS_2, and NiS_3 along crystallographic axes)

This simple reasoning then leaves the most likely effective symmetry as being derived from D_{3h}. In D_{3h} symmetry

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[8] P. S. Shetty and Q. Fernando, *J. Amer. Chem. Soc.*, 1970, 3964.

[9] D. E. Billing, R. J. Dudley, B. J. Hathaway, and A. A. G. Tomlinson, *J. Chem. Soc.* (*A*), 1971, 691.

[10] G. Gliemann, *Ber. Bunsengesellschaft Phys. Chem.*, 1972 **76**, 1008; H. Yersin, Thesis, T.U., Berlin, 1970; W. Tuszynski and G. Gliemann, to be published.

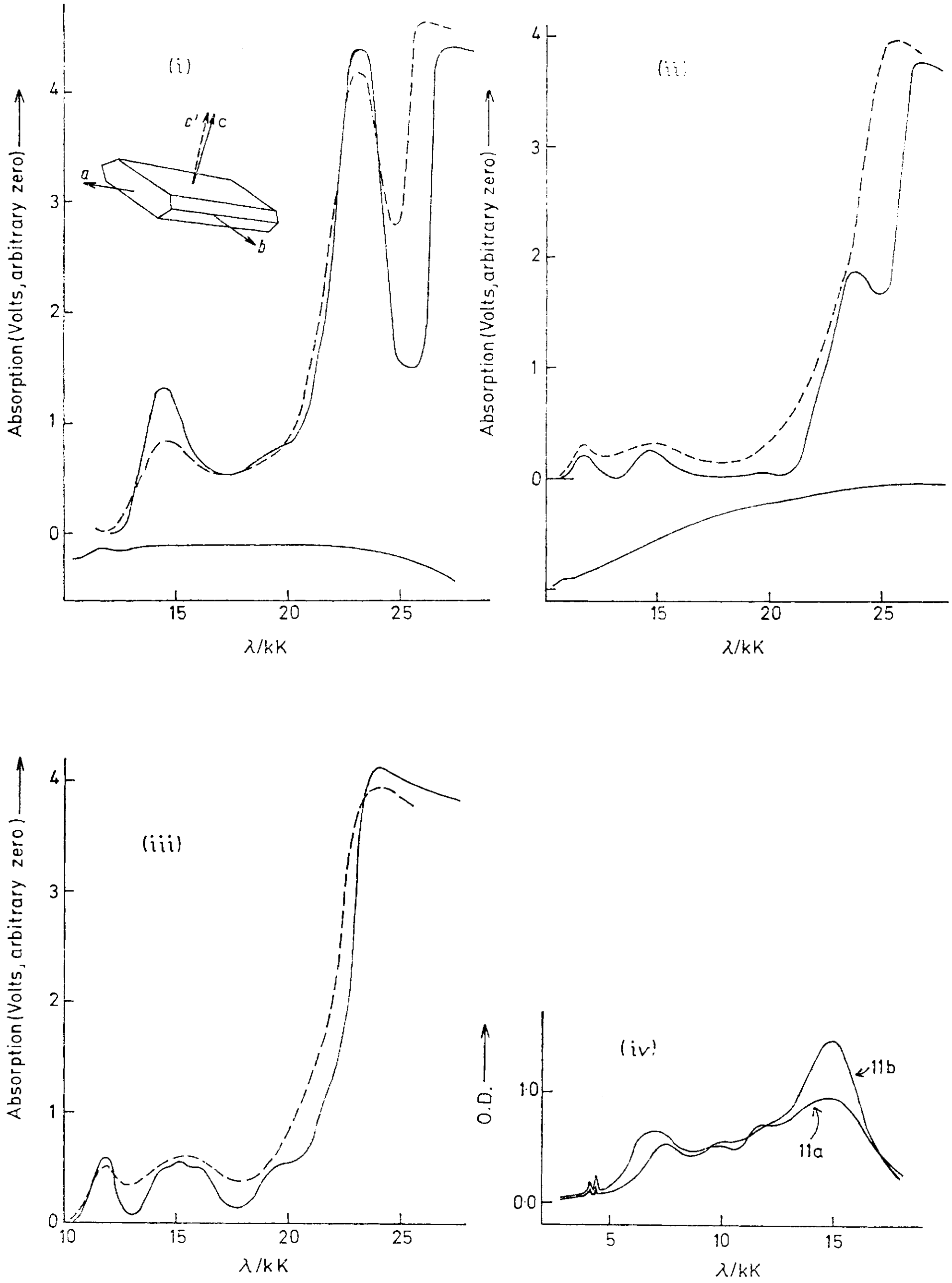

FIGURE 3 Crystal spectra. (i) $E_{\|}\, b$ (inset shows crystal morphology); (ii) $E_{\|}\, a$, both from (001) face; (iii) $E_{\|}$ *ca.* c', (100) face. Baselines shown below (baselines identical with change in temperature), that for (iii) identical to that for (i). —— 4·2 K (nominal); — — — *ca.* 295 K. (iv) Room-temperature spectrum of (001) face between 4 and 16 kK (see text)

there is an electronically degenerate ground state $^3E'$,[4] and this gives rise to two possible ground states, $^3A_1$ and $^3B_2$, in C_{2v} symmetry, for which selection rules are in Table 1. Again, the clear presence of two electronically allowed transitions, at 14·4 and 23·1 kK in z as deduced from the temperature behaviour, eliminates a ground state $^3A_1$ which, instead, should give rise to only vibronically allowed transitions in this direction.

TABLE 1

Selection rules for C_{2v} symmetry derived from D_{3h} ($\sigma_h \rightarrow \sigma_v xz$) for the two possible ground states; + signifies electronically allowed transition, all others allowed vibronically. Selection rules for C_{2v} (from C_{4v}) identical to those for (i)

(i) Ground state $^3A_1$

	x	y	z
$B_2 \leftarrow A_1$	A_2	$A_1{}^+$	B_2
$A_2 \leftarrow$	B_2	B_1	A_2
$B_1 \leftarrow$	$A_1{}^+$	A_2	B_1

(ii) Ground state $^3B_2$

	x	y	z
$A_1 \leftarrow B_2$	A_2	$A_1{}^+$	B_2
$A_2 \leftarrow$	$A_1{}^+$	A_2	B_1
$B_1 \leftarrow$	B_2	B_1	A_2
$B_2 \leftarrow$	B_1	B_2	$A_1{}^+$

An assignment in C_{2v} symmetry with a ground state $^3B_2$ hinges on the attribution of the bands at 14·5 and 23·1 kK to electronically allowed transitions, the former to $^3B_2(P) \leftarrow {}^3B_2$ and the latter to the second $^3B_2(P) \leftarrow {}^3B_2$. It then seems reasonable to assign the band at 23·8 kK in *ca.* parallel to x polarisation to the $^3A_2 \leftarrow {}^3B_2$ transition. Beyond this point it does not appear possible to come to completely unambiguous conclusions due first to the large number of bands found and to absence of vibrational structure at 4·2 K. (In C_{2v} a total of nine bands would be expected, only eight if the intensity of the transition within the split $^3E'$ (D_{3h}) level is too small to allow observation of the band in the measurement range used. This would appear to be the case here; careful infrared measurements between 300 and 4000 cm^{-1} gave no clear indication of the presence of relatively broad bands ascribable to a *d–d* transition.) Two very narrow bands at 4100 and 4400 cm^{-1} did not have the required polarisation behaviour to be considered *d–d* in origin, and are assigned to infrared overtone or combination bands. More seriously there seems to be a trend towards increasing intensity with increasing energy of the bands, presumably owing to gradually increasing intensity-borrowing with charge-transfer states. This means that bands below *ca.* 14 kK are not so clearly attributable to electronically allowed transitions or otherwise. However, despite this the higher intensity of the band at 11·8 kK in *ca.* x polarisation is in agreement with its assignment as the $^3A_2 \leftarrow {}^3B_2$ transition, derived from $^3A_1''$ (D_{3h}). The band at 9·75 kK is then attributed to $^3B_1 \leftarrow {}^3B_2$ and the remaining two, at 7·4 and 6·5 kK, to the split components of $^3E''$ (F) of the parent D_{3h} symmetry.

Assuming that this analysis of the major features of the spectrum is correct, the other three bands remaining must be assigned to spin-forbidden transitions. The high apparent intensities of those at 15·4 and 15·9 are presumably due to their being very close to the spin-allowed transition at 14·4 kK. However, it is not easy to assign these bands to specific transitions.

As might be expected, vibronic selection rules are also operative, as may be seen from the near disappearance of the 19·8 kK band in parallel to a polarisation and also the large drop in intensity of the vibronic residual of the 11·8 kK band in parallel to b polarisation. It would be difficult to defend any vibrational analysis of a molecule as distorted as the present one (and in any case all vibrations are active in C_{2v} symmetry) except that it might be noted that the b_1 vibration appears to be of 'weak' power in allowing vibronic transitions.

Are other assignments possible? Keeping in mind the clearly electronically-allowed transitions at 14·5 and 23·1, the only other possibility of assignment of spin-allowed bands would be one placing the first transition, between the split levels of $^3E'$ (D_{3h}) at, or above, 6·4 kK. This might even be justified from the point of view of the relative intensities given that intensities of all the lower energy transitions are much lower than those of higher ones and that it is not easy to distinguish between electronically allowed and other transitions in this region. However, this assignment would still be in conflict with the relative polarisations of the two bands at 6·4 and 7·4 kK, however unclear these might be. It would also cause difficulties in assigning the split levels of $^3E''$ (D_{3h}), which would, in turn, cause difficulties for the bands deriving from $^3A_1'$, $^3A_2''$ (D_{3h}). Consequently, the assignment given seems to be more in line with the experimental results than this alternative.

TABLE 2

Electronic spectra (kK) and suggested assignment

Transition (Parent D_{3h})	C_{2v}	Single crystal (at 4·2 K)	Reflectance	Acetone solution (ε/l mol^{-1} cm^{-1})
$^3E'$	$^3A_1 \leftarrow {}^3B_2$ $^3B_1 \leftarrow$	6·4	6·4	
$^3E''$	$^3A_2 \leftarrow$	7·4	7·4	6·9 (24)
$^3A_2''$	$^3B_1 \leftarrow$	9·7	*ca.* 9·8	9·7 (22)
$^3A_1''$	$^3A_2 \leftarrow$	11·7	11·4	11·7 (35)
$^3A_2'$	$^3B_2$	14·5	14·5	15·0 (97)
	spin forbidden	15·4 15·9		
b^2E''	$^3B_1 \leftarrow {}^3B_2$	19·8		
	spin forbidden	*ca.* 21·5		
$^3A_2'$	$^3B_2 \leftarrow {}^3B_2$	23·1		
b^3E''	$^3A_2$	23·8	23·5sh	*ca.* 23sh (*ca.* 300)
	c.t.	26·8		

The assignment suggested is shown in Table 2. For an exactly D_{3h} (actually C_{3v}), Ni(NCS)Me$_6$trenNCS,H$_2$O, complex [4] an assignment was suggested with $^3E''(P) < {}^3A_2'$, while that for C_{4v} [Ni(Ph$_2$MeAsO)$_4$NO$_3$]NO$_3$ gave $^3E(P) > {}^3A_2(P)$.[6] The order found in Ni(mpt)$_2$(Me$_2$phen) seems to be roughly between these two. Apart from this there are no large 'crossovers' of levels compared with the crystal-field calculations performed to date [4,5] so far as concerns terms derived from D_{3h} symmetry (unless, of course, $^3A_1 \leftarrow {}^3B_2$ from $^3E'$ ground state in D_{3h} has been lost in the range 6·4—9·7 kK).

On lowering of symmetry, however, the energy-level order taken up is considerably different than that predicted by crystal-field calculations for C_{2v} symmetry.[5] It should be noted, however, that the latter were calculated for α and β angles (see Figure 1) ⩽120°, whereas the present compound has extremely large distortions, S$_1$NiN$_2$ = 130° and S$_1$NiN$_1$ = 147°. This may explain, at least partially, the $^3B_2$ ground state present; a linear extrapolation from the simple crystal-field calculations might indeed give rise to such a ground state. It is not yet possible to give a more detailed explanation except to note that results contrary to calculated energy levels for C_{2v} symmetry have also been found for d^9, although in the latter case these were imputed mainly to π-bonding effects [9,11] as well as distortions.

The form of the spectrum in acetone solution does not greatly differ from that in the solid, with roughly similar intensity ratios for the bands. The implication is that predominantly the same species is present in solution with a similar geometry as in the solid. Ni(mpt)$_2$(*o*-phenanthroline) is believed to give several species in solution.[12]

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[11] B. J. Hathaway, D. E. Billing, R. J. Dudley, R. J. Fereday, and A. A. G. Tomlinson, *J. Chem. Soc.* (*A*), 1970, 806.

[12] M. Shiro and Q. Fernando, *Chem. Comm.*, 1971, 350.