Complexing Properties of α-Nitroketones.[1] Complexes of Nickel(II) and Cobalt(II)

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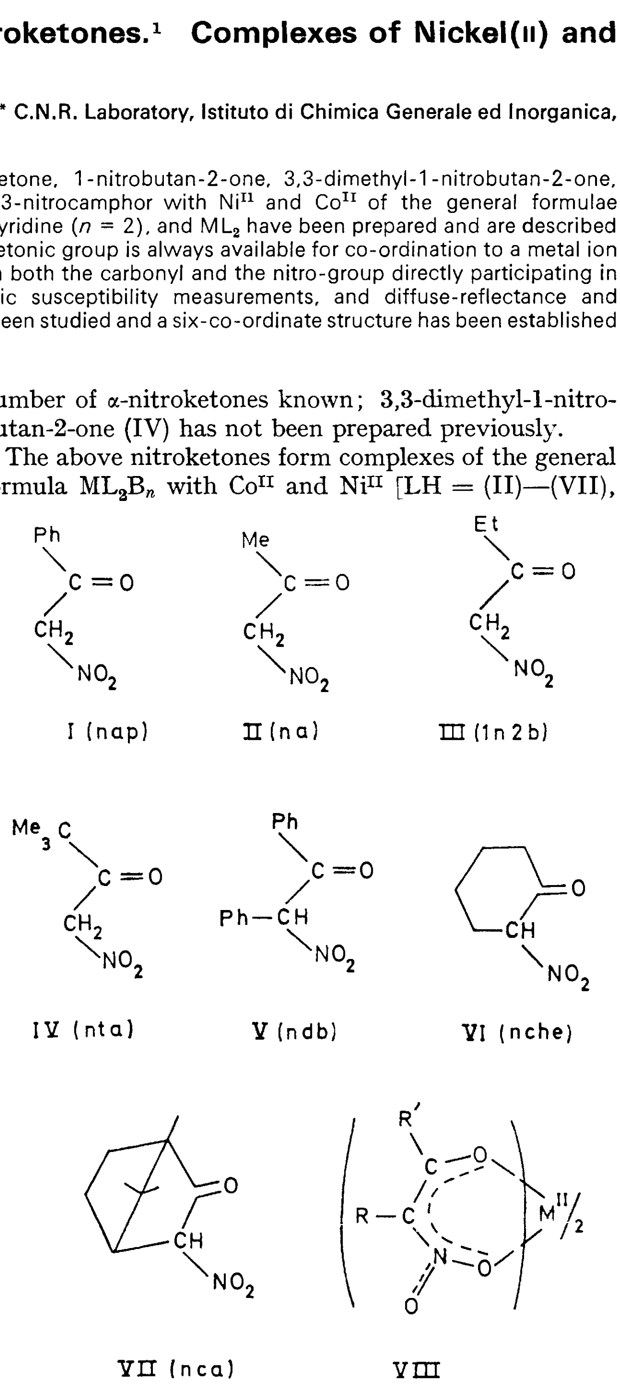
Complexes of the α-nitroketones (LH) nitroacetone, 1-nitrobutan-2-one, 3,3-dimethyl-1-nitrobutan-2-one, α-nitrodeoxybenzoin, 2-nitrocyclohexanone, and 3-nitrocamphor with Ni^{II} and Co^{II} of the general formulae ML_2B_n, where B is water (n = 2 or 3), ethanol or pyridine (n = 2), and ML_2 have been prepared and are described in the present paper. It is shown that the α-nitroketonic group is always available for co-ordination to a metal ion and normally behaves as a bidentate *O*-donor with both the carbonyl and the nitro-group directly participating in the chelation. *X*-Ray powder patterns, magnetic susceptibility measurements, and diffuse-reflectance and solution spectra in the near-i.r.–visible region have been studied and a six-co-ordinate structure has been established for all the complexes examined.

THE participation of an aliphatic nitro-group in the formation of chelate complexes when conjugated with a carbonyl group has been examined previously by studying ω-nitroacetophenone (I) (see Scheme 1).[2] Neutral complexes of formula $M(nap)_2$ were obtained (VIII; M = Mn^{II}, Fe^{II}, Co^{II}, Ni^{II}, and Zn^{II}, R = H, R′ = phenyl group), in which the metal ion behaves as a strongly co-ordinatively unsaturated centre and shows a great tendency to achieve six-co-ordinate, octahedral, or pseudo-octahedral stereochemistry, either by forming associated species or by co-ordination of solvent molecules. More recently the Lewis-acid properties of the chromophore CuO_4 present in $Cu(nap)_2$ have been investigated in detail by the formation of adducts with several mono- and bi-dentate heterocyclic and other nitrogen-bases.[3]

Our investigation of the complexing properties of α-nitroketones has been subsequently extended from (I) to include nitroacetone (II), 1-nitrobutan-2-one (III), 3,3-dimethyl-1-nitrobutan-2-one (IV), α-nitrodeoxybenzoin (V), 2-nitrocyclohexanone (VI), and 3-nitrocamphor (VII). Since (II)—(VII) have at least one hydrogen atom on the carbon carrying the nitro-group, they all behave as monobasic pseudo-acids, as does (I) (in Scheme 1 the abbreviations in parentheses indicate the corresponding anions). The selection of these ligands was partly determined by the restricted number of α-nitroketones known; 3,3-dimethyl-1-nitrobutan-2-one (IV) has not been prepared previously.

The above nitroketones form complexes of the general formula ML_2B_n with Co^{II} and Ni^{II} [LH = (II)—(VII),



SCHEME 1

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[1] Presented in part at the XIII I.C.C.C., Zakopane, Poland, September 14—22nd, 1970.

[2] (*a*) C. Ercolani, I. Collamati, and G. Sartori, *Atti Accad. naz. Lincei, Rend. Classe Sci. fis. mat. nat.*, 1966, **40**, 558; (*b*) M. Bonamico, I. Collamati, C. Ercolani, G. Dessy, and D. J. Machin, *Chem. Comm.*, 1967, 654; (*c*) I. Collamati and C. Ercolani, *J. Chem. Soc.* (*A*), 1969, 1537; (*d*) I. Collamati and C. Ercolani, *ibid*, 1969, 1541.

[3] (*a*) D. Attanasio, I. Collamati, and C. Ercolani, *J. Chem. Soc.* (*A*), 1971, 2516; (*b*) I. Collamati and C. Ercolani, *ibid.*, 1971, 2522.

B = water, ethanol, or pyridine, $n = 2$ or 3]. Some of the water or ethanol adducts can be desolvated to give ML_2 species [LH = (II), (IV), (VI)]. The stereochemistry of the complexes will be discussed, mainly on the basis of their electronic spectra and magnetic properties, in connection with the different electronic inductive effects and steric requirements of the peripheral substituents on the α-nitroketones.

EXPERIMENTAL

Preparation of α-Nitroketones.—Nitroacetone (II) and 1-nitrobutan-2-one (III) were prepared by the methods described by Hurd and Nilson.[4] 2-Nitrocyclohexanone (VI) was prepared *via* the intermediate 1-cyclohexenyl acetate described by Machinskaya,[5] and subsequent nitration of the latter as reported by Griswold.[6]

1,2-Diphenyl-2-nitroethan-1-ol was prepared as described by Bordwell and Garbisch.[7] Its oxidation to α-nitrodeoxybenzoin (V) was carried out as follows. The nitro-alcohol (15 g) was slowly added to a water–glacial acetic acid solution (1 : 1; 90 ml) of potassium dichromate (10·5 g) and sulphuric acid (7·5 ml), and the temperature was raised to 50°. The solution was left to cool slowly and the nitroketone separated as a solid, which was mixed with cold water (300 ml) then filtered off. After crystallisation from isopropyl alcohol, the nitroketone (*ca.* 10 g., 67%) was obtained, m.p. 68—70° (lit.,[8] 73—74°) (Found: C, 69·15; H, 4·5; N, 6·15. Calc. for $C_{14}H_{11}NO_3$: C, 69·7; H, 4·6; N, 5·8%).

3,3-Dimethyl-1-nitrobutan-2-one (IV) was prepared by a method similar to that used for the other aliphatic α-nitroketones.[4] Pivalaldehyde (39·7 g, 50 ml, 0·46 mol) was slowly added, with stirring, to a mixture of nitromethane (28 g, 24·7 ml, 0·46 mol) and water (18·5 ml); a small amount of solid sodium carbonate was added from time to time to keep the medium slightly alkaline. The mixture was stirred for *ca.* 2 h, and then set aside for several hours. The reaction mixture was extracted with ether; the ether extract was dried (Na_2SO_4) and then evaporated. The nitro-alcohol residue was purified by distillation, b.p. 109°, 15 mmHg (yield 15%). The nitro-alcohol (12 g) was added to potassium dichromate (14 g) dissolved in acetic acid (10 ml) containing 10% water. The mixture was stirred and kept at 10—15° while a solution of sulphuric acid (9 ml) and water (4·5 ml) was gradually added. The darkening of the solution showed the progress of the reaction. At the end of the addition, the stirring was continued at room temperature for 2 h; then the mixture was extracted with ether. The low-melting residue was purified by distillation, b.p. 123—126°, 16—17 mmHg (yield 63%).

3-Nitrocamphor (VII) was purchased as the sodium salt (K and K) and was used as such.

Preparation of Complexes. (i) *Adducts of Formula* $ML_2(EtOH)_2$.—A typical experiment for the preparation of the bis-ethanol complexes is as follows. Stoicheiometric amounts of the metal acetate and of the ligand (with a small excess of the latter) in the ratio 1 : 2 were partly suspended and partly dissolved in absolute ethanol, with stirring. Mild heating was used for (V), whereas reactions with (II) were carried out at room temperature. Disappearance of the suspended acetate was followed by the precipitation of the complex. Details for the preparation of the various compounds are as follows.

$Ni(ndb)_2(EtOH)_2$: 1·38 g (5·7 mmol) of (V) in abs. ethanol (25 ml) and 0·705 g (2·85 mmol) of $NiAc_2,4H_2O$ in ethanol (20 ml); yield 75%; recryst., 0·5 g from abs. ethanol (0·3 l).

$Ni(nta)_2(EtOH)_2$: 1·80 g (12·4 mmol) of (IV) and 1·55 g (6·2 mmol) of $NiAc_2,4H_2O$ in abs. ethanol (12 ml); yield 75%; recryst., 1·0 g from abs. ethanol (7 ml).

$Co(nta)_2(EtOH)_2$: 1·80 g (12·4 mmol) of (IV) and 1·55 g (6·2 mmol) of $CoAc_2,4H_2O$ in abs. ethanol (12 ml); yield 71%; recryst. 1·0 g from abs. ethanol (7—8 ml).

(ii) *Adducts of Formula* $ML_2(H_2O)_{2(3)}$.—A procedure very similar to that used for the preparation of the bis-ethanolates was used to prepare several hydrates. Details are as follows.

$Ni(na)_2(H_2O)_2$: 2·78 g (27·0 mmol) and 3·31 g (13·2 mmol) of $NiAc_2,4H_2O$ in 100 ml acetone (with a few drops of water), mild heating; yield 89%; recryst., 1·0 g from *ca.* 1 l of acetone evaporated to 100 ml, with a small amount of (II) to prevent decomposition [or, more conveniently, 1·0 g from abs. ethanol (30 ml)]

$Co(na)_2(H_2O)_2$: 3·20 g (31·1 mmol) and 3·79 g (15·2 mmol) of $CoAc_2,4H_2O$ in 150 ml of acetone (with a few drops of water), mild heating; yield 91%; recryst., 1·0 g from 1 l of acetone in the presence of a small amount of (II).

$Ni(nche)_2(H_2O)_3$: 2·75 g (19·3 mmol) of (VI) and 2·40 g (9·6 mmol) of $NiAc_2,4H_2O$ in 90 ml 95% ethanol; yield 88%; recryst., 1 g from *ca.* 15 ml abs. ethanol with subsequent exposure to atmospheric moisture for 2—3 days; recryst. of $Ni(nche)_2(H_2O)_3$ from dichloroethane gives $Ni(nche)_2(H_2O)_2$.

$Co(nche)_2(H_2O)_3$: 3·65 g (25·0 mmol) of (VI) and 3·10 g (13·0 mmol) of $CoAc_2,4H_2O$ in 70 ml 95% ethanol; yield 75%; recryst., 1 g from *ca.* 15 ml abs. ethanol with subsequent exposure to atmospheric moisture for 2—3 days; $Co(nche)_2(H_2O)_3$ recrystallises unchanged from dichloroethane.

$Ni(nca)_2(H_2O)_2$: 2·01 g (9·2 mmol) of (VII) (Na salt) and 1·15 g (4·6 mmol) of $NiAc_2,4H_2O$ in 80 ml water; yield 72%; recryst., 1 g from methanol–water (1 : 6; 70 ml).

$Co(nca)_2(H_2O)_2$: 2·01 g (9·2 mmol) of (VII) (Na salt) and 1·15 g (4·6 mmol) of $CoAc_2,4H_2O$ in 80 ml water; yield 81%; recryst., 1 g from a mixture of *ca.* 30 ml of methanol–water (1 : 1); a similar preparation of this compound has been reported briefly.[9]

$Ni(nta)_2(H_2O)_2$ and $Co(nta)_2(H_2O)_2$ were obtained from the corresponding bis-ethanol complexes by exposure to atmospheric moisture for *ca.* two weeks.

(iii) *Adducts of Formula* $ML_2(py)_2$.—Most of the bis-pyridine derivatives were obtained by direct reaction of the metal acetate and the appropriate ligand in ethanol–pyridine (4 : 1), pyridine–butanol–heptane, or water–pyridine mixtures. Details are as follows.

$Ni(na)_2(py)_2$: 1·03 g (10·0 mmol) of (II) and 1·24 g (5·0 mmol) of $NiAc_2,4H_2O$ in 15 ml ethanol–pyridine (4 : 1); yield 70%; recryst., 1 g from 26 ml of butanol–pyridine (12 : 1).

$Co(na)_2(py)_2$: 3·47 g (33·7 mmol) of (II) and 4·18 g (16·8 mmol) of $CoAc_2,4H_2O$ in 75 ml ethanol–pyridine (4 : 1); yield 47%; recryst., 1 g from *ca.* 60 ml of butanol–pyridine (10 : 1).

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[4] C. D. Hurd and M. E. Nilson, *J. Org. Chem.*, 1955, **20**, 927.

[5] I. V. Machinskaya, *Zhur. obshchei Khim.*, 1952, **22**, 1159.

[6] A. A. Griswold, *J. Org. Chem.*, 1966, **31**, 357.

[7] F. G. Bordwell and E. W. Garbisch, jun., *J. Org. Chem.*, 1962, **27**, 2322.

[8] J. Meisenheimer and E. Mahler, *Ber.*, 1933, 185.

[9] J. Lifschitz, *Rec. Trav. chim.*, 1922, 627.

Ni(ln2b)$_2$(py)$_2$: 1·02 g (8·7 mmol) of (III) and 1·09 g 4·35 mmol) of NiAc$_2$,4H$_2$O in 15 ml of ethanol–pyridine (4 : 1); yield 80%; recryst., 1 g from *ca.* 55 ml of 95% ethanol.

Co(ln2b)$_2$(py)$_2$: 1·06 g (9·1 mmol) of (III) and 1·13 g (4·55 mmol) of CoAc$_2$,4H$_2$O in 15 ml ethanol–pyridine (4 : 1); yield 86%; recryst., 1 g from *ca.* 50 ml of 95% ethanol.

Ni(ndb)$_2$(py)$_2$: 1·0 g (4·2 mmol) of (V) and 0·51 g (2·1 mmol) of NiAc$_2$,4H$_2$O in 20 ml ethanol–pyridine (4 : 1); yield 65%; recryst., 0·8 g from 60 ml of butanol–pyridine (1 : 11) and 200 ml of heptane.

Co(ndb)$_2$(py)$_2$: 2·0 g (8·3 mmol) of (V) and 1·03 g (4·15 mmol) of CoAc$_2$,4H$_2$O in 40 ml ethanol–pyridine (4 : 1); yield 70%; recryst., 0·85 g from 60 ml of butanol–pyridine (1 : 11) and 150 ml of heptane.

Ni(nta)$_2$(py)$_2$: 0·90 g (6·9 mmol) of (IV) and 0·86 g (3·45 mmol) of NiAc$_2$,4H$_2$O in 5 ml of pyridine then 6 ml butanol and 500 ml of heptane; yield 77%; recryst., 1 g from 65 ml of pyridine + 5 ml of butanol and 320 ml of heptane.

Co(nta)$_2$(py)$_2$: 0·90 g (6·9 mmol) of (IV) and 0·86 g (3·45 mmol) of CoAc$_2$,4H$_2$O in 5 ml of pyridine then 12 ml of butanol and 500 ml of heptane; three types of crystals were obtained from the solution, which can all be formulated as bis-pyridine derivatives of Co(nta)$_2$; the red form 'a' is formed in larger amounts, the orange form 'b' and the deep red form 'c' are formed in limited amounts; recryst. of one or a mixture of these forms usually leads to the 'a' form; recryst., 1 g from 6—7 ml of pyridine + 5 ml of butanol and 300—350 ml of heptane.

Ni(nca)$_2$(py)$_2$: 1·65 g (7·5 mmol) of (VII) (Na salt) and 0·94 g (3·75 mmol) of NiAc$_2$,4H$_2$O in 90 ml water + 1·5 ml of pyridine: yield 97%; recryst., 1 g from 6·5 ml of pyridine + 3 ml of butanol and 33 ml of heptane.

Co(nca)$_2$(py)$_2$: 1·65 g (7·5 mmol) of (VII) (Na salt) and 0·94 g (3·75 mmol) of NiAc$_2$,4H$_2$O in 90 ml water + 1·5 ml of pyridine: yield 90%; recryst., 1 g from 6 ml of pyridine + 3 ml of butanol and 85 ml of heptane.

Ni(nche)$_2$(py)$_2$ and Co(nche)$_2$ (py)$_2$ were obtained by dissolving the corresponding trishydrates in pyridine and then precipitation with butanol and heptane.

Ni(nche)$_2$(py)$_2$: 0·50 g of Ni(nche)$_2$(H$_2$O)$_3$ in 3 ml of pyridine and then 2 ml of butanol + 4 ml of heptane: yield 50%.

Co(nche)$_2$(py)$_2$: 0·60 g of Co(nche)$_2$(H$_2$O)$_3$ in 5 ml of pyridine and then 3·4 ml of butanol + 10 ml of heptane.

(iv) ML$_2$ *Complexes.*—Complexes of formula ML$_2$ (M = Co^{II}, Ni^{II}) were generally obtained from the previously described hydrates or alcohol complexes by heating *in vacuo*. In general, 150—200 mg of the adduct, well ground, were used for the desolvations. The conditions for each compound are as follows:

Ni(na)$_2$: from Ni(na)$_2$(H$_2$O)$_2$ heated at 130°, 10^{-2} mmHg for 45 min;
Co(na)$_2$: from Co(na)$_2$(H$_2$O)$_2$ heated at 120°, 10^{-2} mmHg for 45 min;
Ni(nche)$_2$: from Ni(nche)$_2$(H$_2$O)$_3$ heated at 70°, 10^{-2} mmHg for 90 min;
Co(nche)$_2$: from Co(nche)$_2$(H$_2$O)$_3$ heated at 70°, 10^{-2} mmHg for 90 min;
Ni(nta)$_2$: from Ni(nta)$_2$(EtOH)$_2$ heated at 90°, 10^{-2} mmHg for 60 min;
Co(nta)$_2$: from Co(nta)$_2$(EtOH)$_2$ heated at 80°, 10^{-2} mmHg for 50 min.

Physical Measurements.—Diffuse-reflectance and solution spectra in the near-i.r.-visible region were recorded on a Beckmann DK2 spectrophotometer. Room-temperature magnetic susceptibilities were measured on a Gouy balance, using a magnetic field of *ca.* 7000 G with a nickel chloride solution as calibrant.[10] The variation of the magnetic moment over the temperature range 300—80 K was measured on an apparatus based on a design described previously.[11] *X*-Ray powder spectra were obtained with a Debye powder camera (114·6 mm diam.) with Cu-K_α (Ni-filtered) radiation.

RESULTS

ML$_2$B$_{2(3)}$ and ML$_2$ complexes are listed in Table 1, together with some of their properties and elemental analyses.

Adducts of formula ML$_2$(EtOH)$_2$ in moist air tend to be converted into the corresponding hydrates. The species of formula ML$_2$(H$_2$O)$_n$ (n = 2 or 3) and ML$_2$(py)$_2$ are stable and may be kept in air. The thermal stability of all the adducts studied depends on the nature of the ligand, on the type of metal ion, and on the solvent molecules. However, Ni^{II} adducts are thermally more stable than the corresponding Co^{II} adducts (see melting or decomposition points reported in Table 1), whereas, for the same ligand and metal ion, the thermal stability increases in the order hydrate < ethanol derivative < pyridine derivative. Some of the ethanol or water adducts can be desolvated when heated *in vacuo* to give the parent ML$_2$ species (see Experimental section). On the contrary, none of the bis-pyridine derivatives desolvates before melting or decomposing. Diffuse-reflectance and solution spectra in the near-i.r.-visible region of the Ni^{II} and Co^{II} adducts are given in Tables 2 and 3. The temperature dependence of the magnetic susceptibility of the trishydrates of Ni(nche)$_2$ and Co(nche)$_2$ is reported in Table 4.

The complexes of formula ML$_2$ [M = Co^{II}, Ni^{II}; LH = (II), (IV), (VI)] are all hygroscopic and, on exposure to air, usually tend to form the hydrates. The complexes of (VI) give the trishydrates, M(nche)$_2$(H$_2$O)$_3$, while those of (II) and (IV) give the corresponding dihydrates, M(na)$_2$(H$_2$O)$_2$ and M(nta)$_2$(H$_2$O)$_2$.

DISCUSSION

Complexes of Formula ML$_2$B$_{2(3)}$.—The Ni^{II} complexes are typical of octahedral or pseudo-octahedral high-spin species with respect to colour, magnetic properties, and optical spectra. Room-temperature magnetic moments are mostly within the range 3·1—3·3 B.M. (Table 1). Exceptions are: 3·32 for Ni(nche)$_2$(py)$_2$, 3·35 for Ni(ndb)$_2$(py)$_2$, 3·47 for Ni(ndb)$_2$(EtOH)$_2$, and 3·47 B.M. for Ni(nche)$_2$(H$_2$O)$_3$. Magnetic moments over 3·3 B.M. for octahedral Ni^{II} complexes are frequently quoted in the literature, but they are difficult to explain on the basis of the current theory of magnetism.[12] Ni(nche)$_2$(H$_2$O)$_3$ has been investigated magnetically in the range 300—80 K (Table 4). The magnetic moment is essentially temperature independent, and the Curie–Weiss law is followed (θ = 3).

[10] H. R. Nettleton and S. Sugden, *Proc. Roy. Soc.*, 1939, *A*, **173**, 313.

[11] B. N. Figgis and R. S. Nyholm, *J. Chem. Soc.*, 1959, 331.

[12] A. B. P. Lever, *Inorg. Chem.*, 1965, **4**, 763.

TABLE 1

Some properties and elemental analyses of $ML_2B_{2(3)}$ and ML_2 complexes

				Analyses					
				Calc.			Found		
Compound	Colour	M.p. (°C) *	μ_{eff} (B.M.) †	C	H	N	C	H	N
$Ni(na)_2(H_2O)_2$	Green	215	3·23	24·1	4·0	9·4	24·3	4·0	9·2
$Ni(na)_2(py)_2$	Green	190	3·19	45·65	4·3	13·3	45·9	4·65	13·15
$Ni(1n2b)_2(py)_2$	Green	209	3·16	48·15	4·9	12·5	48·1	5·3	12·5
$Ni(nche)_2(H_2O)_3$	Yellow-green	145	3·47	36·2	5·55	7·05	36·6	5·8	7·0
$Ni(nche)_2(H_2O)_2$	Green	140	3·20	37·9	5·3	7·35	37·9	5·3	7·3
$Ni(nche)_2(py)_2$	Yellow-green	178	3·32	52·6	5·2	11·2	52·9	5·3	10·9
$Ni(ndb)_2(EtOH)_2$	Yellow	135	3·47	60·7	5·05	4·45	60·7	5·0	4·6
$Ni(ndb)_2(py)_2$	Yellow	188	3·35	65·1	4·3	8·0	64·9	4·5	8·1
$Ni(nta)_2(EtOH)_2$	Green	139	3·24	43·8	7·3	6·2	43·95	7·1	6·2
$Ni(nta)_2(H_2O)_2$	Green	129	3·24	37·65	6·3	7·5	37·2	5·9	7·8
$Ni(nta)_2(py)_2$	Olive-green	175	3·16	52·3	5·95	11·1	52·7	6·0	10·9
$Ni(nca)_2(H_2O)_2$	Pale green	240	3·21	49·25	6·8	5·75	48·9	6·7	5·6
$Ni(nca)_2(py)_2$	Olive-green	205	3·16	59·1	6·3	9·2	59·0	6·2	9·25
$Co(na)_2(H_2O)_2$	Orange	156	4·83	24·1	4·0	9·4	24·2	4·0	9·3
$Co(na)_2(py)_2$	Red	174	4·86	45·65	4·3	13·3	45·8	4·6	13·0
$Co(1n2b)_2(py)_2$	Red	177	4·90	48·15	4·9	12·5	48·1	4·7	12·5
$Co(nche)_2(H_2O)_3$	Red	125	4·97	36·2	5·55	7·05	36·1	5·5	7·1
$Co(nche)_2(py)_2$	Brown	150	4·90	52·6	5·2	11·2	52·4	5·05	11·4
$Co(ndb)_2(py)_2$	Red-brown	155	4·86	65·1	4·3	8·0	65·3	4·5	8·5
$Co(nta)_2(EtOH)_2$	Orange	122	4·87	43·8	7·3	6·2	44·1	7·0	5·6
$Co(nta)_2(H_2O)_2$	Red-brown	90		37·65	6·3	7·5	37·3	6·1	7·0
$Co(nta)_2(py)_2$ ' a '	Red	150	4·97	52·3	5·95	11·1	52·1	6·2	11·3
$Co(nta)_2(py)_2$ ' b '	Orange	148		52·3	5·95	11·1	51·8	5·9	11·2
$Co(nta)_2(py)_2$ ' c '	Deep red	150		52·3	5·95	11·1	52·0	6·1	10·5
$Co(nca)_2(H_2O)_2$	Red	158	4·97	49·25	6·8	5·7	49·7	6·9	6·2
$Co(nca)_2(py)_2$	Orange-red	175	4·71	59·1	6·3	9·2	59·3	6·0	9·0
$Ni(na)_2$	Yellow-green			27·4	3·05	10·65	26·8	3·3	10·2
$Ni(nta)_2$	Green			41·5	5·75	8·05	41·0	5·8	8·3
$Ni(nche)_2$	Green			41·85	4·65	8·15	41·4	5·1	8·6
$Co(na)_2$	Brown			27·4	3·05	10·65	26·7	3·2	10·15
$Co(nta)_2$	Brown			41·45	5·75	8·05	41·2	6·0	8·4
$Co(nche)_2$	Brown			41·85	4·65	8·15	40·7	5·05	8·1

* M.p. = melting or decomposition point; some of the complexes lose the solvent before melting. † Calculated from the formula $\mu_{eff} = 2{\cdot}84\ (\chi_A\ .\ T)^{\frac{1}{2}}$; diamagnetic corrections were calculated from Pascal's constants.

TABLE 2

Diffuse-reflectance and solution spectra of the complexes $NiL_2B_{2(3)}$ in the region 7·0—23·0 kK

		kK (nm, ε) *			
Compound	Medium	ν_1		ν_2	
$Ni(na)_2(H_2O)_2$	Solid, refl.	10·0 (1000)	*13·3* (750)	16·65 (600)	*22·2* (450)
$Ni(na)_2(py)_2$	Solid, refl.	10·8 (925)	*13·25* (755)	17·7 (565)	*22·2* (450)
	Pyridine	10·0 (1000, 9·25)	*13·0* (770, 2)	16·7 (600, 14·3)	
$Ni(1n2b)_2(py)_2$	Solid, ref.	10·9 (920)	*13·0* (770)	17·9 (560)	*21·8* (460)
	Pyridine	9·9 (1010, 9·95)	*12·8* (780, 3)	16·55 (605, 15·1)	
$Ni(nta)_2(H_2O)_2$	Solid, refl.	9·1 (1100)	*13·3* (750)	15·6 (640)	*21·0* (475)
$Ni(nta)_2(EtOH)_2$	Solid, refl.	9·7 (1030)	*13·3* (750)	15·9 (630)	*21·8* (460)
$Ni(nta)_2(py)_2$	Solid, refl.	10·65 (940)	*13·0* (770)	17·7 (565)	*22·2* (450)
	Pyridine	10·0 (1000, 9·9)	*12·8* (780, 3)	16·8 (595, 15·3)	*21·8* (460, 50)
$Ni(ndb)_2(EtOH)_2$	Solid, refl.	9·3 (1080)	*13·3* (750)	16·3 (615)	*20·0* (500)
$Ni(ndb)_2(py)_2$	Solid, refl.	9·3 (1080)	*12·9* (775)	16·7 (600)	*20·0* (500)
	Pyridine	9·9 (1010, 9·15)	*12·8* (780, 4)	16·6 (600, 21·4)	*20·0* (500, 60)
$Ni(nche)_2(H_2O)_2$	Solid, refl.	9·1 (1100)		16·4 (610)	*20·8* (480)
$Ni(nche)_2(H_2O)_3$	Solid, refl.	8·9 (1125)	*13·0* (770)	15·8 (635)	*20·2* (495)
$Ni(nche)_2(py)_2$	Solid, refl.	9·7 (1030)	*12·5* (800)	17·1 (595)	*20·4* (490)
	Pyridine	9·75 (1025, 13·2)	*12·8* (780, 4)	17·1 (595, 20·2)	*20·8* (480, 70)
$Ni(nca)_2(H_2O)_2$	Solid, refl.	9·5 (1050)		15·7 (635)	*20·0* (500)
$Ni(nca)_2(py)_2$	Solid, refl.	10·5 (950)		17·4 (575)	*20·8* (480)
	Pyridine	9·85 (1015, 8·8)	*12·8* (780, 2)	16·5 (605, 13)	*20·4* (490, 17·7)

* Absorptions given in italics indicate shoulders.

Diffuse-reflectance spectra of the Ni^{II} complexes and their spectra in pyridine solution (Table 2) in the region 7·0—23·0 kK show in all cases two main absorptions of low intensity ($\varepsilon < 20$), at 9·0—11·0 kK (ν_1) and 15·5—18·0 kK (ν_2), associated with the two lowest-energy triplet–triplet transitions expected for Ni^{II} in a weak octahedral ligand field. Shoulders are also observed *ca.* 13 and 20—22 kK, the latter being on the tail of a very intense absorption located at higher energy. Whereas the band *ca.* 13 kK is probably associated with a triplet–singlet transition, it is uncertain whether the shoulder at 20—22 kK should be assigned to the third triplet–triplet transition, its energy being slightly lower (by *ca.* 2·0—2·3 kK) than that predicted on the basis of the energy of ν_1 and ν_2. The energy of ν_1 (coincident with the ligand-field strength parameter Δ in O_h symmetry) increases regularly within the series $NiL_2(H_2O)_2 < NiL_2(EtOH)_2 < NiL_2(py)_2$ at fixed L. Accordingly, the room-temperature magnetic moments decrease in the same order, as would be predicted from the expression [13]

$$\mu_{eff} = \mu_{s.o.}(1 - 4\lambda/\Delta)$$

where $\mu_{s.o.}$ is the spin-only magnetic moment and λ is the spin–orbit coupling constant for Ni^{II} in the complexes formed.

TABLE 3

Diffuse-reflectance and solution spectra of the complexes $CoL_2B_{2(3)}$ in the region 7·0—23·0 kK

Compound	Medium	kK (nm, ε) *			
$Co(na)_2(H_2O)_2$	Solid, ref.	9·1 (1100)	*19·1* (525)	*23·5* (425)	
$Co(na)_2(py)_2$	Solid, refl.	10·3 (975)	*18·7* (535)	*23·5* (425)	
	Pyridine	9·35 (1070, 8·5)	*18·2* (550, 60)	*19·1* (525, 96)	
$Co(1n2b)_2(py)_2$	Solid, refl.	10·25 (975)	*18·7* (535)	*22·2* (450)	
	Pyridine	9·3 (1075, 9·15)	*18·2* (550, 67)	*19·1* (525, 95)	
$Co(nta)_2(H_2O)_2$	Solid, refl.	8·7 (1150)	*18·2* (550)	*21·0* (475)	
$Co(nta)_2(EtOH)_2$	Solid, refl.	8·9 (1120)	*18·3* (545)	*23·3* (430)	
$Co(nta)_2(py)_2$ ' a '	Solid, refl.	10·3 (970)	*18·2* (550)	*19·4* (515)	*22·2* (450)
$Co(nta)_2(py)_2$ ' b '	Solid, refl.	10·0 (1000)	*18·2* (550)	*19·4* (515)	*22·2* (450)
$Co(nta)_2(py)_2$ ' c '	Solid, refl.	9·1 (1100)	*18·2* (550)	*19·4* (515)	*21·5* (465)
	Pyridine	9·3 (1075, 9·25)	*19·4* (515, 82)	*21·8* (460, 150)	
$Co(ndb)_2(py)_2$	Solid, refl.	9·5 (1055)	*18·2* (550)	*20·0* (500)	
	Pyridine	9·4 (1065, 8·0)			
$Co(nche)_2(H_2O)_3$	Solid, refl.	8·5 (1165)	*18·9* (530)	*20·4* (490)	*22·0* (450)
$Co(nche)_2(py)_2$	Solid, refl.	9·6 (1040)	*17·9* (560)	*22·0* (450)	
	Pyridine	9·5 (1055, 12·5)	*17·6* (570, 40)	*21·8* (460, 150)	
$Co(nca)_2(H_2O)_2$	Solid, refl.	8·75 (1140)	20·4 (490)		
$Co(nca)_2(py)_2$	Solid, refl.	9·9 (1025)	*17·6* (570)	*21·0* (475)	
	Pyridine	9·4 (1065, 4·5)	*19·6* (510, 100)	21·0 (475, 120)	

* Absorptions given in italics indicate shoulders.

TABLE 4

Temperature dependence of the magnetic susceptibility of the trishydrates of $Ni(nche)_2$ and $Co(nche)_2$

$Ni(nche)_2(H_2O)_3$ ($\theta = +3$ K) [a]			$Co(nche)_2(H_2O)_3$ ($\theta = +7$ K) [a]		
T (K)	$10^6\chi_{Ni}$ [b]	μ_{eff} (B.M.)	T (K)	$10^6\chi_{Co}$ [b]	μ_{eff} (B.M.)
300	5030	3·49	301	10,240	4·99
285	5212	3·47	285·5	10,674	4·96
277	5316	3·46	280	10,861	4·95
263·5	5497	3·42	264·5	11,326	4·92
250·5	5705	3·40	250·5	11,791	4·88
236	6068	3·40	236	12,412	4·86
220	6508	3·40	222	13,095	4·84
204·5	6975	3·40	210·5	13,715	4·83
187	7675	3·40	187·5	15,143	4·79
169·5	8505	3·41	171	16,508	4·76
152·5	9413	3·40	152	18,494	4·75
133·5	10,787	3·41	131·5	21,504	4·76
113	12,965	3·43	113·5	24,762	4·75
101·5	14,469	3·44	103·5	26,934	4·74
94·5	15,610	3·44	93	29,634	4·71
79·5	18,358	3·43	79	35,020	4·73

[a] Calculated by expressing the Curie–Weiss law as $\chi = k(T + \theta)^{-1}$. [b] In c.g.s. units.

Although in the spectra of the bis-pyridine adducts $NiL_2(py)_2$, the position of ν_1 ranges between 9·3 and 10·9 kK for the solid, considerably less significant variations occur in the spectra taken in pyridine solution (range for ν_1 : 9·75—10·0 kK). Since L carries either electron-withdrawing or electron-releasing groups in the series $NiL_2(py)_2$, it is concluded that the variation in the ligand field acting on the metal ion, as is determined by the change in substituents attached to the α-nitroketonic groups, is not such that it is revealed by a significant variation in the energy of the ligand-field spectrum. A similar observation was made by Graddon [14] for a series of solid bis-pyridine derivatives of Ni^{II}–β-diketone chelates, which show spectra with a narrow range for ν_1 (10·1—10·4 kK). The spectra in solution reported for this series of complexes are unfortunately restricted to those observed in benzene for bis(acetylacetonato)bis(pyridine)nickel(II) $[Ni(acac)_2(py)_2]$ and bis(benzoylacetonato)bis(pyridine)nickel(II) $[Ni(bzac)_2(py)_2]$, which have close values of ν_1 at 9·75 and 9·65, respectively.[15] From the energy of ν_1 in the spectra of the Ni^{II} complexes, the chelating systems originating from the β-diketones and the α-nitroketones can be roughly estimated to occupy similar positions in the spectrochemical series.

The spectral results (Table 2) show that $Ni(nche)_2(H_2O)_3$ is pseudo-octahedral, and the magnetic behaviour within the temperature range 300—80 K is as expected for a magnetically diluted complex of that symmetry. We prefer the formula $[Ni(nche)_2(H_2O)_2]H_2O$ for this complex, since the co-ordination of all three molecules of water to Ni^{II} would require that one of the two α-nitroketonic groups act as a monodentate and the second as a bidentate ligand, which seems highly improbable. With only two molecules of water entering

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[13] J. Lewis and R. G. Wilkins, ' Modern Coordination Chemistry,' Interscience, New York, 1957, p. 427.

[14] D. P. Graddon, *Co-ordination Chem. Rev.*, 1969, **4**, 1.

[15] J. T. Hashagen and J. P. Fackler, *J. Amer. Chem. Soc.*, 1965, **87**, 2821.

the co-ordination sphere of Ni^{II}, the third one must necessarily be dispersed in the crystal lattice. It cannot, however, be eliminated from the complex to give the corresponding dihydrate, since both at atmospheric pressure and *in vacuo*, all water molecules are simultaneously eliminated on heating to give the corresponding anhydrous bis(nitrocyclohexanonato)nickel(II) [$Ni(nche)_2$] (see later). The dihydrate, also pseudo-octahedral (from the magnetic and spectral properties, Tables 1 and 2), could nevertheless be obtained by recrystallisation of [$Ni(nche)_2(H_2O)_2$],H_2O from dichloroethane.

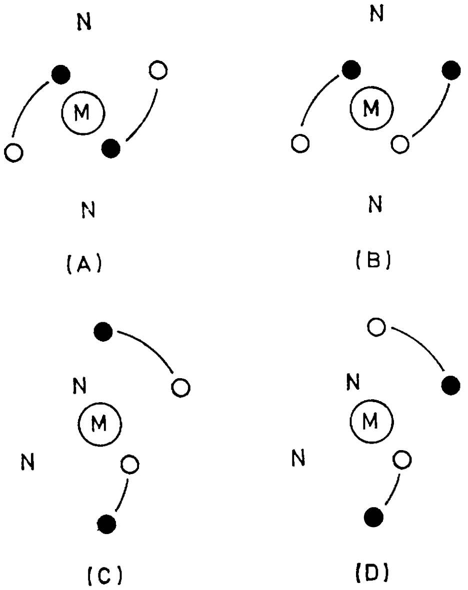
Among the Co^{II} species listed in Table 1, $Co(nta)_2(py)_2$ is the only one which has been isolated in more than one crystalline form, *i.e.*, ' a ', ' b ', and ' c '. Among these, the deep red form ' c ' is the only one which is isomorphous with the corresponding Ni^{II} compound. Forms ' a ' and ' b ' are neither isomorphous with ' c ' nor with one another.

An octahedral or pseudo-octahedral structure may be assumed for all the Co^{II} complexes on the basis of the established isomorphism with the corresponding Ni^{II} complexes, as well as from their spectral and magnetic properties. From Table 3 it can be seen that all the Co^{II} complexes, including forms ' a ', ' b ' and ' c ' of $Co(nta)_2(py)_2$, show diffuse-reflectance spectra and spectra in solution (for the bispyridine derivatives) with an absorption band, of low intensity ($\varepsilon < 20$) for the spectra taken in pyridine, having the maximum point between 8·0 and 10·0 kK. Almost undetectable shoulders are also observed in the region 17·0—23·0 kK on the tail of a very intense higher-energy absorption.

The room-temperature magnetic moments of the Co^{II} complexes (Table 1) range mostly, as expected for an octahedral structure, between 4·8 and 5·0 B.M., with only the exception of $Co(nca)_2(py)_2$ (4·71 B.M.). The temperature dependence of the magnetic moment of $Co(nche)_2(H_2O)_3$ is given in Table 4. On decreasing the temperature within the range 300—80 K, a 0·26 B.M. reduction of the magnetic moment was observed, with a θ value of 25°. These data agree well with those observed for the series of octahedral Co^{II} complexes of formula $Co(nap)_2B_2$ ($B =$ water, ethanol, pyridine) previously described.[2c] Both the variation in the magnetic moment and the θ value appear to be smaller than those observed for $Co(nap)_2$, which is octahedral and antiferromagnetic,[2c] and for other CoL_2 species described later in this paper.

From any of the α-nitroketones examined in the present paper, complexes of the type ML_2B_n can be obtained, at least in the form of bispyridine adducts. An important observation is that the α-nitroketonic group is always available for co-ordination irrespective of the nature of the peripheral substituents. Furthermore, in any of the complexes studied it behaves as a bidentate chelating system through the direct participation in chelation of both the carbonyl and the nitro-group; chromophores MO_4O_2 and MO_4N_2 are produced, depending on the type of co-ordinated solvent molecules. The chelating ring in the above complexes should be similar to that found in the complexes of ω-nitroacetophenone [see structure (VIII)] and verified in the *X*-ray crystal structure of $Cu(nap)_2$.[2b]

The existence of forms ' a ', ' b ' and ' c ' of $Co(nta)_2(py)_2$ raises the question of what is the arrangement of the ligands around Co^{II} in each of these forms, and in general in the Co^{II} and Ni^{II} complexes dealt with in the present paper. The octahedral complexes $Co(nap)_2(py)_2$ and $Ni(nap)_2(py)_2$ were found by *X*-ray data to be isomorphous to one another [2c] and *trans*.[16] This result agrees with the assumption that a *trans*-configuration is in general more favourable than a *cis* one, and helps in assigning a probable *trans*-octahedral configuration to the parent complexes, with an axial co-ordination of the solvent molecules (A, Scheme 2). If the isomer ' b ' of $Co(nta)_2(py)_2$ and the corresponding isomorphous Ni^{II} complex are assigned the *trans*-configuration (A), then the isomers ' a ' and ' c ' can be assigned one of the alternative structures (B), (C), or (D).



SCHEME 2

Forms (A)—(D) are drawn taking into account the asymmetric structure of the α-nitroketones.

Complexes of Formula ML_2.—Diffuse-reflectance and solution spectra of $Co(na)_2$ and $Ni(na)_2$ in dichloroethane in the region 7·0—25·0 kK are shown in the Figure. The position and the intensity of the near-i.r. and visible absorptions in the spectra of both metal ions, together with the fact that for the same metal ion the spectrum in solution corresponds to that of the solid, unequivocally indicate that the two complexes have an octahedral or pseudo-octahedral structure in both media. The spectra of the Co^{II} and Ni^{II} complexes of

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[16] P. Porta, unpublished results.

3,3-dimethyl-1-nitrobutan-2-one and 2-nitrocyclohexanone (Table 5) allow the same conclusions to be drawn about their structure. It is worth noting that both for Ni^{II} and Co^{II} the spectra are practically superimposable on one another by changing the α-nitroketone [compare also the spectra of Ni(nap)$_2$ and Co(nap)$_2$.] Assuming that also in these complexes, as previously generally observed in this paper (see also ref. 2a—2d, 3a, 3b) the α-nitroketonato-group operates as a bidentate *O*-donor, the ML$_2$ species, if mononuclear, should be four-co-ordinate. The raising of the co-ordination number from four to six therefore suggests the formation of intermolecular contacts allowing occupation of the fifth and sixth co-ordination positions of the central metal ion. No evidence has been found of the formation of solution species of co-ordination

TABLE 5

Diffuse-reflectance and solution spectra of NiL$_2$ and CoL$_2$ complexes in the region 6·0—25·0 kK

Compound	Medium	kK (nm, ε) [a]				
Ni(na)$_2$	Solid, refl.	9·1 (1100)	*13·3* (750)	15·4 (650)	*22·2* (450)	*b*
	Dichloroethane	8·9 (1125, 8·7)	*13·15* (760, 6·9)	15·2 (660, 11·3)	*22·2* (450, 48)	
Ni(nta)$_2$	Solid, refl.	8·95 (1115)	*12·9* (775)	15·5 (645)	*21·5* (465)	*b*
	Benzene	8·7 (1150, 11·8)	*12·9* (775, 10·2)	14·7 (680, 15)	*21·3* (470, 40)	
Ni(nche)$_2$	Solid, refl.	8·8 (1135)	*13·0* (770)	15·3 (655)	*21·0* (475)	*b*
	Dichloroethane	8·8 (1135, 11)	*13·1* (765, 7·6)	14·9 (670, 12·3)	*21·0* (475, 25)	
Ni(nap)$_2$	Solid, refl.	8·85 (1130)	*12·9* (775)	15·25 (655)	*21·0* (475)	*c*
	Benzene	8·9 (1125, 5·7)	*12·9* (775, 4)	15·15 (660, 7·5)	*21·0* (475, 39)	
Co(na)$_2$	Solid, refl.	8·5 (1175)	*19·0* (525)			*b*
	Dichloroethane	8·5 (1175, 8·2)	*18·2* (550, 83)	*19·4* (515, 95)		
Co(nta)$_2$	Solid, refl.	8·6 (1165)	*18·2* (550)	*19·4* (515)		*b*
	Benzene	8·35 (1200, 12·9)	*17·9* (560, 124)	*18·9* (530, 180)		
Co(nche)$_2$	Solid, refl.	8·6 (1160)	*19·1* (525)			*b*
	Dichloroethane	8·4 (1190, 10·3)	*18·2* (550, 94)	*19·6* (510, 195)		
Co(nap)$_2$	Solid, refl.	8·3 (1200)	*18·0* (555)	*20·0* (500)		*d*
	Benzene	8·35 (1200, 12)	*17·6* (570, 110)	*20·0* (500, 240)		

[a] Absorptions given in italics indicate shoulders. [b] This work. [c] Ref. 2*a*. [d] Ref. 2*c*.

TABLE 6

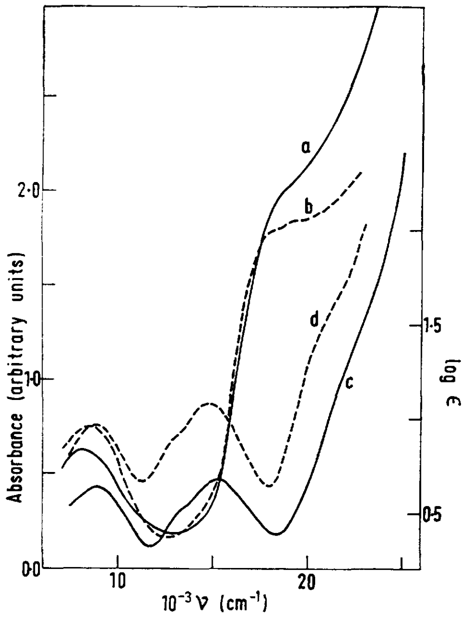
Temperature dependence of the magnetic susceptibility of the ML$_2$ species *

Ni(na)$_2$			Ni(nta)$_2$			Ni(nche)$_2$		
T (K)	$10^6\chi_{Ni}$	μ_{eff} (B.M.) †	*T* (K)	$10^6\chi_{Ni}$	μ_{eff} (B.M.) †	*T* (K)	$10^6\chi_{Ni}$	μ_{eff} (B.M.) †
297	4250	3·19	299·5	4033	3·12	300·5	4458	3·29
290·5	4434	3·22	290·5	4170	3·12	289·5	4551	3·26
268·5	4579	3·15	289·5	4154	3·11	274·5	4783	3·25
245·5	4869	3·10	279	4323	3·11	248·5	5248	3·24
227·5	5284	3·11	261	4531	3·09	223	5759	3·21
213	5583	3·10	247·5	4789	3·09	201·5	6223	3·18
196	6028	3·08	231	5062	3·06	185	6687	3·16
182·5	6385	3·06	215·5	5279	3·02	167	7291	3·14
164	6975	3·03	200·5	5608	3·01	150·5	7941	3·10
145	7709	3·00	184	6010	2·98	128·5	9009	3·06
127·5	8539	2·97	164	6588	2·96	111	9985	2·99
111·5	9525	2·92	145·5	7199	2·95	98	10,983	2·95
102·5	10,162	2·90	122·5	8300	2·86	78·5	13,003	2·86
92·5	11,012	2·87	105·5	9200	2·76			
77·5	12,558	2·80	94·5	9818	2·72			
			79	11,098	2·65			
Co(na)$_2$			Co(nta)$_2$			Co(nche)$_2$		
296	9690	4·82	300	9241	4·73	301	8913	4·67
289·5	9818	4·79	290	9479	4·71	285·5	9258	4·62
277	10,115	4·75	285·5	9611	4·70	276·5	9452	4·58
252·5	10,838	4·71	277·5	9796	4·68	264	9732	4·56
229	11,730	4·66	261·5	10,324	4·66	250	10,141	4·52
210·5	12,580	4·62	246·5	10,720	4·62	234	10,722	4·50
199·5	13,175	4·60	231·5	11,221	4·58	220	11,282	4·47
174·5	14,790	4·56	212·5	12,066	4·54	205·5	11,928	4·45
164·5	15,555	4·54	198	12,911	4·53	189	12,789	4·42
145·5	17,340	4·51	181·5	13,756	4·49	169	14,038	4·37
126·5	19,550	4·47	164	14,891	4·44	153	15,243	4·33
113	21,420	4·42	145·5	16,291	4·37	132	17,138	4·27
103	23,163	4·39	126·5	18,350	4·32	113·5	19,334	4·20
92·5	25,160	4·33	105·5	21,043	4·23	100·5	21,358	4·16
79·5	28,135	4·25	95·5	22,759	4·18	91·5	23,037	4·12
			79·5	25,664	4·05	79·5	26,008	4·08

* Diamagnetic corrections were calculated from Pascal's constants. † Calculated from the formula $\mu_{eff} = 2{\cdot}84\,(\chi_A \,.\, T)^{\frac{1}{2}}$.

number lower than six either in equilibrium with these latter or alone. Furthermore, the spectra of the same complex taken in the same solvent, at different concentrations, always agreed with the Lambert–Beer law.

Evidence supporting molecular association is also provided by the magnetic behaviour of the solid ML_2 species. Magnetic data are summarised in Tables 6 and 7. The Ni^{II} complexes show magnetic moments, within the temperature range 300—80 K, which are temperature dependent with a quenching of μ_{eff} of 0·39, 0·47, and 0·43 B.M. for $Ni(na)_2$, $Ni(nta)_2$, and $Ni(nche)_2$, respectively. The corresponding θ values are 32, 47, and 38 K. Both $\Delta\mu_{eff}$ and θ are in all cases only slightly smaller than those observed for $Ni(nap)_2$ (see Table 7); however, the temperature dependence of the magnetic susceptibility definitely reveals the presence of an antiferromagnetic interaction, which evidently comes from the formation of associated species, in agreement with the above spectral conclusions.



Diffuse-reflectance and solution spectra of a, $Co(na)_2$, reflectance; b, solution in dichloromethane; c, $Ni(na)_2$, reflectance; d, solution in dichloromethane

TABLE 7

Summary of the magnetic data

Compound	μ_{eff} (B.M.) (300 K)	μ_{eff} (B.M.) (80 K)	$\Delta\mu_{eff}$ (B.M.)	θ (K)	Ref.
$Ni(na)_2$	3·19	2·80	0·39	32	*b*
$Ni(nta)_2$	3·12	2·65	0·47	47	*b*
$Ni(nche)_2$	3·29	2·86	0·43	38	*b*
$Ni(nap)_2$	3·11	2·57	0·54	60	2c
$Co(na)_2$	4·82	4·25	0·57	30	*b*
$Co(nta)_2$	4·73	4·06	0·67	38	*b*
$Co(nche)_2$	4·67	4·08	0·59	26	*b*
$Co(nap)_2$	4·66	4·12	0·54	34	2c
$Co(nap)_2(H_2O)_2$	4·89	4·48	0·41	21	2c
$Co(nap)_2(EtOH)_2$	4·93	4·58	0·35	25	2c
$Co(nap)_2(py)_2$	4·84	4·51	0·33	20	2c
$Co(nche)_2(H_2O)_3$	4·99	4·73	0·26	7	2

[a] Calculated by expressing the Curie–Weiss law as $\chi = k\,(T + \theta)^{-1}$. [b] This work.

For the CoL_2 complexes the room-temperature magnetic moments are definitely below those of most of the corresponding magnetically diluted pseudo-octahedral adducts. The decrease in the magnetic moment within the interval 300—80 K is much more consistent than that usually observed for magnetically normal octahedral Co^{II} complexes, and definitely larger, as are the θ values, than for $Co(nche)_2(H_2O)_3$ and the series $Co(nap)_2B_2$ (B = water, ethanol, pyridine) (Table 7). This behaviour is in keeping with the occurrence of appreciable antiferromagnetic interactions in all the CoL_2 complexes examined.

Molecular-weight measurements carried out on $Co(nap)_2$ and $Ni(nap)_2$ proved that they are tetrameric and trimeric, respectively, in benzene solution.[2c] For the Co^{II} and Ni^{II} complexes examined here, the formation of the corresponding hydrated species during molecular-weight measurements noticeably affected the reproducibility of the results, which generally provided, for both metal ions, values of 2·0—2·5 for the association factor. Although these results substantially support the existence of associated species also in solution, as suggested indirectly by the correspondence of the electronic spectra of the solution to those of the solid, it has not been possible to establish which kind of oligomeric species actually occur for complexes of ligands other than ω-nitroacetophenone. It must be pointed out, however, that the association factor cannot be 2, as this would not explain the formation of six-co-ordinated species. Much higher values would, on the other hand, be in contrast with the appreciable solubility observed for the ML_2 species in non-co-ordinating solvents. Hence, values of the association factor very close to those found for $Co(nap)_2$ and $Ni(nap)_2$ appear to be most likely for the ML_2 species formed by the other α-nitroketones. In view of the common structural and electronic features displayed by the α-nitroketonato- and β-diketonato-groups and the close correspondence previously pointed out [2c] of the association factors found for the Co^{II} and Ni^{II} complexes of acetylacetone and ω-nitroacetophenone, the molecular associated species observed for $Ni(nap)_2$ and $Co(nap)_2$ were assumed [2c] to be built up in a way similar to that found for the complexes of acetylacetone, with intermolecular interactions taking place through the sharing of oxygen atoms already involved in the chelation. It seems reasonable to accept the occurrence of the same type of intermolecular contacts in the ML_2 species discussed here.

The results given above for the ML_2 species show that both in the solid state and in solution the tendency to six-co-ordination (through self-association) on the part of the metal ion (previously shown by the formation of adducts) is equally strong within each of the two series of complexes NiL_2 and CoL_2, irrespective of the nature of the substituents on the α-nitroketones examined. Thus neither steric requirements nor electronic inductive effects of the ligands are such as to break the intermolecular contacts to form species of lower co-ordination numbers. Such a uniform behaviour towards molecular association is not paralleled by that exhibited by the corresponding complexes of the β-diketones. The tendency to form associated species was found to vary gradually within the large series of Ni^{II} complexes of formula NiL_2 prepared from β-diketones with varying substituents.[17] Some β-diketones are known to form only green paramagnetic pseudo-octahedral polynuclear Ni^{II} species, while other β-diketones provide only red diamagnetic square-planar mononuclear species. Cases are also known of β-diketones for which both polynuclear and mononuclear forms have been isolated and characterised. Similar behaviour is displayed by the analogous series of the Co^{II}–β-diketonates. It is concluded that the uniform tendency shown by ML_2 complexes of α-nitroketones to form associated species is clearly more marked than in the corresponding complexes of the β-diketones.

Undoubtedly, the bonding features of the nitro-group in the α-nitroketonic system contribute strongly to make the π-electron delocalisation of the chelating ring in the complexes formed [Scheme 1, (VIII)] considerably more extensive than in the corresponding β-diketonic system. Two main considerations arise from this, which help to explain the above results: the over-all σ–π electronic system present in the α-nitroketonic group evidently operates as a ' cushion ' partially absorbing and quenching the effects produced on the central metal ion by the different substituents. On the other hand, it stabilises the net negative charge better than in the β-diketonic group and this, as previously postulated [3b] for the complexes of ω-nitroacetophenone, allows greater retention of negative charge on the chelating system, hence increasing the residual positive charge on the metal ion and the co-ordinative unsaturation of the latter in the complexes formed. As a direct consequence, the intermolecular association forces should (i) be similar within each series of Ni^{II}– and Co^{II}–α-nitroketonates, and (ii) be stronger than those acting in the associated forms of the corresponding Ni^{II}– and Co^{II}–β-diketonates.

We thank Mr. M. Gardini for experimental assistance on some of the magnetic measurements.

[1/1201 *Received*, 12*th July*, 1971]

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