Transition-metal Complexes of the Macrocyclic Ligand 5,12-Dimethyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene

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The macrocyclic ligand 5,12-dimethyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene (L^1) has been prepared as its dihydroperchlorate salt by the reaction of ethane-1,2-diamine monohydroperchlorate with methyl vinyl ketone. A *transoid* arrangement of the imine linkages has been confirmed by a crystallographic study on *trans*-[CoL^1(SCN)$_2$]SCN·H$_2$O. A number of metal(II) complexes [ML^1][ClO$_4$]$_2$ (M = Ni, Cu, Co, or Zn) have been prepared. In addition a series of octahedral cobalt(III) complexes of the general type *trans*-[CoL^{1}X]$^{n+}$ (X = Cl$^-$, Br$^-$, NO$_2^-$, SCN$^-$, or NH$_3$) and *cis*-[CoL^1(aa)]$^{n+}$ (aa = CO$_3^{2-}$ or acac$^-$) have been synthesised. Two separate isomers of *trans*-[CoL^{1}Cl$_2$][ClO$_4$]$_2$ have been identified corresponding to the *rac*- and *meso*-diastereoisomers resulting from the asymmetric secondary nitrogen donors. The co-ordination chemistry of L^1 is discussed and i.r. and *d–d* electronic spectra are reported.

RECENTLY Kolinski and Korybut-Daszkiewicz [1] reported the preparation of a new tetra-azacyclotetradecadiene macrocyclic ligand by the reaction of the monohydroperchlorate salt of ethane-1,2-diamine with methyl vinyl ketone. This synthesis is an extension of the procedure first described by Curtis and Hay [2] for the preparation of the macrocyclic ligand 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetra-azacyclotetradeca-4, 11-diene, L^2, (IV). The reaction of monohydroperchlorate salts of ethane-1,2-diamine with αβ-unsaturated carbonyl compounds appears to be stereospecific. Thus the *transoid* isomer of L^2 appears to be formed exclusively.[2,3a] In view of the similar preparative methods Kolinski and Korybut-Daszkiewicz have provisionally assigned the *transoid* imine structure (I) rather than *cisoid* structure (II) to the ligand L^1. Recent crystallographic work [3b] has now confirmed this view and the ligand is therefore 5,12-dimethyl-1,4,8,11-tetra-azacyclotetradeca-

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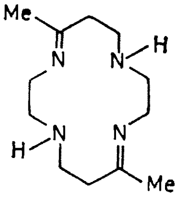
[1] R. A. Kolinski and B. Korybut-Daszkiewicz, *Bull. Acad. polon. Sci.*, 1969, **17**, 13.

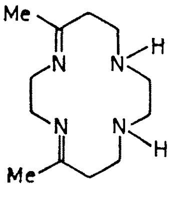
[2] N. F. Curtis and R. W. Hay, *Chem. Comm.*, 1966, 524.

[3] (*a*) R. W. Hay, G. A. Lawrance, and N. F. Curtis, *J.C.S. Perkin I*, 1975, 591; (*b*) R. J. Restivo, J. Horney, and G. Ferguson, *J.C.S. Dalton*, submitted for publication.

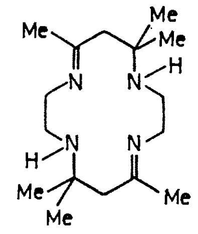
4,11-diene, (I). The present paper discusses some aspects of the co-ordination chemistry of this new macrocyclic ligand. The only metal complex which has previously been described [1] is $[NiL^1][ClO_4]_2$.



(I)
(ligand abbreviation L^1)



(II)



(III)
(ligand abbreviation L^2)

EXPERIMENTAL

5,12-*Dimethyl*-1,4,8,11-*tetra-azacyclotetradeca*-4,11-*diene Dihydroperchlorate*.—The macrocyclic Schiff base was prepared by a variation of the method first described by Kolinski and Korybut-Daszkiewicz.[1] Aqueous perchloric acid (45 cm^3, 35%) was added dropwise, with stirring, to cooled (ice-bath) aqueous ethane-1,2-diamine (37 cm^3, 50%). The solution of the ethane-1,2-diamine monohydrogen perchlorate was evaporated to dryness with an air stream. The resulting white solid was then dried in a vacuum desiccator. (*Solutions containing amine perchlorates should not be evaporated to dryness by heating otherwise extremely violent explosions may result.*) After drying, the ethane-1,2-diamine monohydrogen perchlorate was broken up and mixed with methanol (250 cm^3). The solution was cooled in an ice–salt bath and the flask purged with nitrogen. Methyl vinyl ketone (22 cm^3) in dry methanol (35 cm^3) was then added dropwise with vigorous stirring, the temperature being kept below 0 °C during the addition. After addition of the methyl vinyl ketone the mixture was stirred for a further 4 h, the temperature being allowed to slowly rise to room temperature. The white precipitate which formed was filtered off, washed with ice-cold methanol then ether, and dried *in vacuo*; yield 25.1 g (60% based on ethane-1,2-diamine). The dihydroperchlorate salt can be recrystallised from hot methanol if necessary, but the material is of a sufficient purity for the subsequent preparations, m.p. 108—109 °C (lit.,[1] 109—110 °C) (Found: C, 33.5; H, 6.1; N, 12.9. Calc. for $C_{12}H_{24}N_4{\cdot}2HClO_4$: C, 33.9; H, 6.2; N, 13.2%).

5,12-*Dimethyl*-1,4,8,11-*tetra-azacyclotetradeca*-4,11-*dienenickel*(II) *Perchlorate*.—Nickel(II) acetate tetrahydrate (0.3 g) was heated in methanol–water (300 cm^3; 1 : 1 v/v) with a slight excess of ligand $L^1{\cdot}2HClO_4$ (0.5 g) on a water-bath for 30 min; the solution was then filtered whilst hot. The filtrate was reduced to *ca.* 2 cm^3 (rotary evaporator) and methanol (15 cm^3) was added. The yellow product crystallised when the mixture was cooled in ice; it was filtered off, washed with ice-cold methanol then ether, and dried *in vacuo* (yield 0.47 g, 80%) (Found: C, 30.0; H, 5.1; N, 11.6. $C_{12}H_{24}Cl_2N_4NiO_8$ requires C, 29.9; H, 5.0; N, 11.6%).

5,12-*Dimethyl*-1,4,8,11-*tetra-azacyclotetradeca*-4,11-*dienecopper*(II) *Perchlorate*.—Copper(II) carbonate (0.7 g) was suspended in water (30 cm^3) and a slight excess of the ligand $L^1{\cdot}2HClO_4$ (1.1 g) was added. The mixture was heated on a water-bath for 30 min and the red-purple solution was filtered whilst hot; it was then evaporated to dryness on a rotary evaporator. The resulting solid was dissolved in the minimum volume of hot methanol. Cooling in ice gave reddish purple crystals, which were filtered off, washed with ice-cold methanol and then ether, and finally dried in *vacuo*; yield 0.6 g (45%) (Found: C, 29.4; H, 5.0; N, 11.3. $C_{12}H_{24}Cl_2CuN_4O_8$ requires C, 29.6; H, 5.0; N, 11.5%).

5,12-*Dimethyl*-1,4,8,11-*tetra-azacyclotetradeca*-4,11-*dienecobalt*(II) *Perchlorate*.—Cobalt(II) perchlorate hexahydrate (0.75 g) was mixed with a slight excess of $L^1{\cdot}2HClO_4$ (0.65 g) in methanol (300 cm^3). The mixture was heated on a water-bath for *ca.* 20 min, under a nitrogen atmosphere to limit oxidation, filtered whilst hot, and cooled in an ice-bath. The fine brown crystalline *product* was filtered, washed with ice-cold methanol then ether, and finally dried *in vacuo*; yield 0.25 g (30%) (Found: C, 29.8; H, 5.25; N, 11.5. $C_{12}H_{24}Cl_2CoN_4O_8$ requires C, 29.9; H, 5.0; N, 11.6%).

5,12-*Dimethyl*-1,4,8,11-*tetra-azacyclotetradeca*-4,11-*dienezinc*(II) *Perchlorate Monohydrate*.—Zinc(II) perchlorate hexahydrate (0.5 g) was dissolved in water (10 cm^3) and a slight excess of $L^1{\cdot}2HClO_4$ (0.45 g) in methanol (15 cm^3) added. The mixture was heated on a water-bath for 30 min, filtered whilst hot, and the solvent removed on a rotatory evaporator. The white *product* was recrystallised from the minimum volume of hot methanol by cooling in an ice-bath; after it had been filtered off it was washed with ice-cold methanol and dried *in vacuo*; yield 0.4 g (70%) (Found: C, 28.4; H, 5.0; N, 10.9. $C_{12}H_{26}Cl_2N_4O_9Zn$ requires C, 28.45; H, 5.2; N, 11.05%).

trans-*Dichloro*(5,12-*dimethyl*-1,4,8,11-*tetra-azacyclotetradeca*-4,11-*diene*)*cobalt*(III) *Perchlorate*.—*Isomer* (a). Sodium tris(carbonato)cobaltate(III) (0.8 g) and $L^1{\cdot}2HClO_4$ (0.8 g) were mixed in methanol–water (30 cm^3, 1 : 1 v/v) and heated on a steam-bath until effervescence ceased (*ca.* 10 min). Concentrated hydrochloric acid (15 cm^3) was added to the red solution and the volume reduced on a steam-bath. The green *product* obtained when the mixture was cooled in an ice-bath was filtered off and recrystallised from hot methanol. All fractions isolated from the recrystallisation gave identical i.r. spectra. Isomer (*a*), therefore, appears to be formed almost exclusively by this route; yield 0.6 g (65%).

Isomer (b). A hot solution of cobalt(II) acetate tetrahydrate (3.5 g) in methanol (100 cm^3) was added to $L^1{\cdot}2HClO_4$ (6.4 g). The mixture was heated on a water-bath for 30 min, and filtered whilst hot, and then cooled. The filtrate was diluted with methanol–water (100 cm^3; 1 : 1 v/v) and air was passed through it for 20 h. The methanol was removed on a rotary evaporator and concentrated hydrochloric acid (40 cm^3) was added to the dull red solution. The green *product* was isolated by slow evaporation on a steam-bath followed by cooling in an ice-bath, and was recrystallised from *ca.* 6M-hydrochloric acid. Two fractions of isomer (*b*) were isolated by cooling the hydrochloric acid solution; an initial fraction was obtained when the mixture was set aside for *ca.* 1 h in an ice-bath. A second fraction was obtained, when methanol (2—3 cm^3) was added to the mixture and the latter set aside in a refrigerator for several days. Concentration of the filtrate on a steam-bath, followed by cooling and the addition of methanol gave an additional fraction identified as isomer (*a*). Isomer (*b*) constituted some 75—80% of the recrystallised material and isomer (*a*) some 20—25%. Isomer (*b*) is less soluble in aqueous hydrochloric acid (8M) than isomer (*a*), but is more soluble in methanol. It was, therefore, possible to use these solubility differences to separate the two isomers. The total yield of isomer (*a*) and isomer (*b*) was 4.5 g (90%) [Found: C, 32.0; H, 5.4; N, 12.3 isomer (*a*): C, 32.0; H, 5.45; N, 12.3 isomer (*b*). $C_{12}H_{24}Cl_3CoN_4O_3$ requires C, 31.8; H, 5.3; N, 12.35%].

Isomer (*b*) was used for the subsequent preparations of the *trans*-isomers, the substitution of chloride by other ligands being readily accomplished.

trans-*Dibromo*(5,12-*dimethyl*-1,4,8,11-*tetra-azacyclotetradeca*-4,11-*diene*)*cobalt*(III) *Perchlorate Monohydrate*.—A solution of *trans*-[CoL^{1}Cl$_2$][ClO$_4$] (0.2 g) in a 10% methanolic solution of hydrobromic acid (25 cm^3) was evaporated to a small volume (*ca.* 3 cm^3) on a steam-bath. The bright green *product* was isolated by cooling the mixture in an ice-bath; it was recrystallised from hot methanol, washed with ice-cold methanol and ether, and dried *in vacuo* (yield 0.2 g, 80%) (Found: C, 25.5; H, 4.4; N, 9.8. $C_{12}H_{26}Br_2ClCoN_4O_3$ requires C, 25.7; H, 4.7; N, 10.0%).

trans-(5,12-*Dimethyl*-1,4,8,11-*tetra-azacyclotetradeca*-4,11-*diene*)*dinitrocobalt*(III) *Perchlorate*.—A solution of *trans*-[CoL^{1}Cl$_2$][ClO$_4$] (0.23 g) in methanol (40 cm^3) was heated with a slight excess of sodium nitrite (0.06 g) on a water-bath for 20 min. The brown solution was filtered whilst hot, and cooled in an ice-bath. The *product* crystallised as small orange-brown crystals, which were filtered off, washed with ice-cold methanol then ether, and dried *in vacuo* (yield 0.16 g, 65%) (Found: C, 30.6; H, 5.05; N, 17.7. $C_{12}H_{24}ClCoN_6O_8$ requires C, 30.4; H, 5.1; N, 17.7%).

trans-*Diammine*(5,12-*dimethyl*-1,4,8,11-*tetra-azacyclotetradeca*-4,11-*diene*)*cobalt*(III) *Perchlorate Chloride*.—To a solution of *trans*-[CoL^{1}Cl$_2$][ClO$_4$] (0.3 g) dissolved in the minimum volume of hot methyl cyanide was added a few drops of concentrated ammonia (5 g, 0.88). The solution became orange after being stirred for *ca.* 10 min. Several drops of an ethanolic solution of lithium perchlorate were then added and the solution was cooled in an ice-bath. The yellow *product* which crystallised was filtered off and recrystallised from the minimum volume of hot water by cooling in ice and addition of methanol. The *product* was filtered, washed with methanol and ether, and dried *in vacuo* (yield 0.2 g, 60%) (Found: C, 29.95; H, 6.2; N, 17.0. $C_{12}H_{30}Cl_3CoN_6O_4$ requires C, 29.7; H, 5.8; N, 17.3%).

trans-(5,12-*Dimethyl*-1,4,8,11-*tetra-azacyclotetradeca*-4,11-*diene*)*di-isothiocyanatocobalt*(III) *Thiocyanate Dihydrate*.—To a solution of *trans*-[CoL^{1}Cl$_2$][ClO$_4$] (0.25 g) in hot aqueous methanol (30 cm^3) was added an excess of solid potassium thiocyanate. The mixture was heated on a water-bath for *ca.* 20 min and the resulting red solution was filtered whilst hot. The filtrate was cooled in a refrigerator for *ca.* 2 days when red crystals of the *product* formed; these were filtered off, washed with cold methanol then ether, and dried *in vacuo* (yield 0.15 g, 55%). The i.r. spectrum of the complex exhibited no perchlorate absorption, but bands due to ionic thiocyanate (Found: C, 36.95; H, 5.7; N, 20.0. $C_{15}H_{28}CoN_7O_2S_3$ requires C, 36.7; H, 5.3; N, 19.95%).

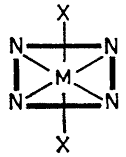
cis-*Carbonato*(5,12-*dimethyl*-1,4,8,11-*tetra-azacyclotetradeca*-4,11-*diene*)*cobalt*(III) *Perchlorate Sesquihydrate*.—Trisodium tris(carbonato)cobaltate(III) (1.0 g) and L^1·2HClO$_4$ (1.0 g) were mixed in methanol–water (40 cm^3; 1 : 1 v/v) and heated on a steam-bath until effervescence ceased. The dark solution was filtered whilst hot. Methanol and ether were then added to the solution which was then cooled in an ice-bath for several hours when the pink product crystallised. It was filtered off and recrystallised from hot aqueous methanol with final cooling in a refrigerator for *ca.* 1 day (yield 0.36 g, 40%) (Found: C, 33.15; H, 5.6; N, 11.9. $C_{13}H_{27}ClCoN_4O_{8.5}$ requires C, 33.2; H, 5.8; N, 11.9%).

cis-*Acetylacetonato*(5,12-*dimethyl*-1,4,8,11-*tetra-azacyclotetradeca*-4,11-*diene*)*cobalt*(III) *Perchlorate–Propan*-2-*ol*.—To a solution of *trans*-[CoL^{1}Cl$_2$][ClO$_4$] (0.4 g) in hot methanol (30 cm^3) was added acetylacetone (0.2 g) and a few drops of concentrated ammonia solution. The solution was heated on a steam-bath for *ca.* 30 min, and the red solution adjusted to a pH of *ca.* 7 with perchloric acid; it was then filtered whilst hot. The methanol was removed on a rotary evaporator and the residue dissolved in propan-2-ol. Ether was added to the solution until it was turbid and then it was placed in a refrigerator overnight when well formed red needles of the *product* crystallised. The crystals were washed with ice-cold methanol then ether and dried *in vacuo* (yield 0.3 g, 70%). The i.r. spectrum confirmed the presence of propan-2-ol of crystallisation (Found: C, 37.8; H, 6.0; N, 8.6. $C_{20}H_{40}Cl_2CoN_4O_{11}$ requires C, 37.6; H, 5.8; N, 8.7%).

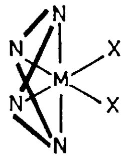
I.r. spectra were determined as KBr discs using a Perkin-Elmer 457 spectrophotometer. Visible spectral measurements were carried out with a Perkin-Elmer 402 instrument.

RESULTS AND DISCUSSION

Crystallographic work[3b] on *trans*-[CoL^1(SCN)$_2$]SCN·H$_2$O has confirmed that the ligand has the *trans*-imine structure (I) and that the complex has a *trans*-stereochemistry. On co-ordination to a metal ion two interconvertible diastereoisomers (*rac* or *meso*) are possible depending upon the relative disposition of the N–H bonds with respect to each other. In addition, each of these diastereoisomers could adopt either a planar or a folded geometry on co-ordination to a metal ion (IV) and (V). The reaction of ethane-1,2-diamine monohydroperchlorate with mesityl oxide and methyl vinyl ketone appears to be completely stereospecific giving only the *trans* macrocyclic di-imines. It is, therefore, interesting that Myers and Rose[4] have recently described the synthesis of an analogous 16-



(IV)



(V)

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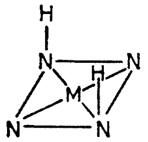
[4] J. F. Myers and N. J. Rose, *Inorg. Chem.*, 1973, **12**, 1238.

membered macrocyclic ligand by the reaction of propane-1,3-diamine and methyl vinyl ketone in the presence of both nickel(II) and hydrogen ions, which has the *cis*-configuration (VI).[5] As the nickel complex isolated represented only 13% of the total nickel present it is possible that the *trans*-isomer also occurs in this reaction.

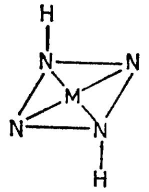
Metal Complexes.—The macrocycle L^1 with two amino donor groups present in a 14-membered ring acts as a tetradentate ligand. The metal(II) complexes are readily prepared, and isolated as their perchlorate salts. The metal(II) perchlorate complexes are four-co-ordinate and the cobalt(III) compounds six-co-ordinate. The spectroscopic properties of the complexes, discussed below, are consistent with an essentially square-planar geometry for the metal(II) perchlorate salts, and a *trans*-arrangement of the unidentate ligands in the octahedral cobalt(III) derivatives $[CoL^1X_2]^{n+}$. This latter point has been confirmed for L = NCS by a crystal structure analysis.[3b] Co-ordination of bidentate ligands such as acac⁻ or CO_3^{2-} also occurs to give the complexes $[CoL^1(CO_3)]^+$ and $[CoL^1(acac)]^{2+}$.

The nickel(II) complex of L^1 does not favour axial co-ordination, even in the presence of strongly co-ordinating ligands such as thiocyanate. Similar observations have been made with L^2. Several explanations have been offered to account for this behaviour. One is the strong tendency of the secondary amine protons to hydrogen bond to the anions in both the solid and solution states.[6,7] The second is the tendency toward decreased co-ordination in the axial positions of six-co-ordinate nickel(II) complexes which contain strong in-plane fields.[8] Steric crowding of the axial sites may also be a contributing factor, although this seems unlikely since the L^1 is less crowded than the L^2 and both ligands readily form cobalt(III) complexes containing axial ligands.

Two isomers have been reported for both the nickel(II) [9] and cobalt(III) [10] complexes of L^2. These isomers have been shown [9] to correspond to the two possible orientations of the N–H bonds (*racemic* or *meso*) of the secondary nitrogen donors. No attempt has been made to separate the isomers of the metal(II) compounds, however two diastereoisomers of *trans*-$[CoL^1Cl_2][ClO_4]$ have been identified. These diastereoisomers [designated isomer (*a*) and isomer (*b*)] have very similar properties and spectra to the related compounds prepared from the L^2 ligand.[10] The reaction of $Na_3[Co(CO_3)_3]$ with $L^1\cdot2HClO_4$ appears to give isomer (*a*) almost exclusively while the reaction of the diene dihydroperchlorate with cobalt(II) acetate gives predominantly isomer (*b*). It is probable that the reaction which yields isomer (*a*) proceeds *via* an intermediate *cis*-carbonato-complex in which the macrocycle adopts a folded configuration with a specific geometry at the secondary nitrogen centres. Under acidic conditions it is likely that this geometry is retained in the final *trans*-product. Treatment of *cis*-$[CoL^1(CO_3)]^+$ with hydrochloric acid gave isomer (*a*) of *trans*-$[CoL^1Cl_2]^+$ (*ca.* 100% from the i.r. spectra) providing confirmatory evidence for the above scheme. Base hydrolysis of isomer (*a*) of *trans*-$[CoL^1Cl_2]$ followed by treatment with hydrochloric acid to regenerate the dichloro-complex gave isomer (*b*) and a trace of isomer (*a*) (from i.r. spectra). In basic solutions the N–H protons will undergo rapid exchange to give the most thermodynamically stable configuration at the secondary nitrogen centres. Isomer (*a*) thus represents the nitrogen configuration optimum for folded co-ordination designated α, while isomer (*b*) represents the optimum for planar co-ordination designated β. [This nomenclature is consistent with that adopted for complexes of L^2 (ref. 11) and also for related cyclic tetra-amines.[12-14]] In view of the (*a*) $\longrightarrow$ (*b*) isomerisation in basic solution, it appears that isomer (*a*) of *trans*-$[CoL^1Cl_2]^{2+}$ is the *meso*-diastereoisomer (VI) while isomer (*b*) is the *rac*-diastereoisomer (V).



(IV)
rac-diastereoisomer



(V)
meso-diastereoisomer

I.r. Spectra.—The i.r. spectra of the ligand dihydroperchlorate and its metal complexes were recorded as potassium bromide discs. The principal absorption bands are listed in Table 1. The i.r. spectra of the complexes all show bands at *ca.* 3 200 cm⁻¹ ν(NH), and *ca.* 1 660 cm⁻¹ (ν(C⁚N). Complexes formulated as hydrates show typical ν(OH) and δ(HOH) bands.

The skeletal vibrations of the macrocycle, in the 750—1 500 cm⁻¹ region, reflect changes in the geometry of the macrocycle. A comparison of the spectra of $[CoL^1(aa)]^{n+}$ (aa = CO_3^{2-} or acac⁻) with that of $[CoL^1Cl_2]^+$ reflects the differences between the folded geometry in the former complexes and the planar geometry in the latter, when due allowances are made for anion absorptions. Bands observed in the chloro-complex are either not observed in the folded complexes or are shifted somewhat in their positions. Bands at 1 660 and 1 630 cm⁻¹ ν(CO nonbonded) and 1250, 810, and 755 cm⁻¹ [δ(CO) + ν(CO)] in the carbonato-complex are consistent with chelate carbonate.[10,15]

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[5] J. F. Myers and C. H. L. Kennard, *J.C.S. Chem. Comm.*, 1972, 77.

[6] M. F. Bailey and I. E. Maxwell, *Chem. Comm.*, 1966, 908.

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[9] N. F. Curtis, Y. M. Curtis, and H. K. J. Powell, *J. Chem. Soc.*, 1966, 1015.

[10] N. Sadasivan, J. A. Kernohan, and J. F. Endicott, *Inorg. Chem.*, 1967, **4**, 770.

[11] N. F. Curtis, *J.C.S. Dalton*, 1972, 1357.

[12] N. F. Curtis, *J. Chem. Soc.*, 1964, 2644.

[13] N. F. Curtis and G. W. Reader, *J. Chem. Soc.* (*A*), 1971, 1771.

[14] D. F. Cook, N. F. Curtis, and R. W. Hay, *J.C.S. Dalton*, 1973, 1160.

[15] K. Nakamoto, 'Infrared Spectra of Inorganic and Coordination Compounds,' John Wiley, New York, 1963.

The chelated acetylacetonate ligand has characteristic absorption bands at 1 565 and 1 525 cm^{-1}.

The unidentate ligands in the inner co-ordination sphere of cobalt(III) show characteristic absorption bands in some of the complexes (Table 1). The isothiocyanato-structure in $[CoL^1(NCS)_2]^+$ is consistent with the observed C–N and C–S frequencies.[16,17] The i.r. spectra of the two isomeric forms of $[CoL^1Cl_2]^+$ [(*a*) and (*b*)] are very similar, but differences occur in band intensities and multiplets in the region of the skeletal vibrations of the ligand (1 100—1 500 cm^{-1}). Similar differences have been reported for the analogous derivatives of L^2 (ref. 10) and in the two isomers of $[CuL^2]^{2+}$.[18]

TABLE 1

Prominent i.r. absorption bands (in cm^{-1})

Compound	ν_{N-H}	$\nu_{C=N}$	$\nu_{ClO_4^-}$	Other ligand bands
$L^1\cdot 2HClO_4$	3 160s	1 665s	1 100vs,b 625s	
$[NiL^1][ClO_4]_2$	3 220s	1 650s	1 095vs,b 627s	
$[CuL^1][ClO_4]_2$	3 240s	1 668s	1 100vs,b 628s	
$[CoL^1][ClO_4]_2$	3 240s	1 668s	1 100vs,b 627s	
$[ZnL^1][ClO_4]_2\cdot H_2O$	2 225s	1 665s	1 090vs,b 626s	
cis-$[CoL^1(CO_3)][ClO_4]\cdot 1\frac{1}{2}H_2O$	3 160s,b	Masked	1 095vs,b 626s	1 660vs 1 630vs (ν_{CO} nonbonded) 1 250m 810m ($\delta_{CO} + \nu_{CC}$) 755m
cis-$[CoL^1(acac)][ClO_4]_2$	3 240s	1 660s	1 905vs,b 626s	1 565s 1 525s (ν_{CO})
trans-$[Co(a\text{-}L^1)Cl_2][ClO_4]$	3 225s	1 660s	1 100vs,b 628s	
trans-$[Co(b\text{-}L^1)Cl_2][ClO_4]$	3 225s	1 662s	1 905vs,b 628s	
trans-$[CoL^1Br_2][ClO_4]\cdot H_2O$	3 220s	1 656s	1 095vs,b 626s	
trans-$[CoL^1(NO_2)_2][ClO_4]$	3 180s	1 658s	1 090vs,b 624s	1 400vs $\nu_{asym}(NO_2)$ 3 141vs $\nu_{sym}(NO_2)$ 823s $\delta(NO_2)$
trans-$[CoL^1(NH_3)_2][ClO_4]_3$	3 300s	1 655s	1 095vs,b 626s	3 140vs,b 3 060vs,b ν_{NH_3} 5 165w 825m
trans-$[CoL^1(SCN)_2][SCN]$	3 160s,b	1 660s	Not observed	2 100vs (C=N, co-ord) 2 040vs (C=N, ionic) 840m (S–C, co-ord)

vs = Very strong; s = strong; m = medium; w = weak; b = broad

TABLE 2

Visible and u.v. spectra †

Compound [a]	*d–d* Transitions [b]			Charge transfer [b]	
$L^1\cdot 2HClO_4$					225 (370)
$[ZnL^1][ClO_4]_2\cdot H_2O$					240 (800)
$[NiL^1][ClO_4]_2$		446 (89)		279 (4.9×10^3)	227 (1.3×10^4)
$[CuL^1][ClO_4]_2$		508 (87)		265sh (5.1×10^3)	244 (6.3×10^3)
$[CoL^1][ClO_4]_2$		460sh (54)	325sh (225)	268sh (600)	218 (2.0×10^3)
trans-$[Co(a\text{-}L^1)Cl_2][ClO_4]$ [c]	622 (42)	428 (69)	320sh	268sh (1.2×10^4)	235 (1.7×10^4)
trans-$[Co(a\text{-}L^1)Cl_2][ClO_4]$ [d]	616 (47)	435 (49)	320sh	Not determined	
trans-$[Co(b\text{-}L^1)Cl_2][ClO_4]$ [d]	616 (45)	435 (58)	320sh	217 (2.4×10^4)	230 (2.0×10^4)
trans-$[CoL^1Br_2][ClO_4]\cdot H_2O$ [d]	656 (65)	375sh	(Masked)	313 (1.4×10^4)	<200 ($\sim 10^5$)
trans-$[CoL^1(NO_2)_2][ClO_4]$	438 (205)	353 (3.8×10^3) [e]		260 (1.4×10^4)	211 (2.0×10^4)
trans-$[CoL^1(NH_3)_2][ClO_4]_3$	448 (80)	334 (110)			218 (3.3×10^4)
trans-$[CoL^1(SCN)_2][SCN]$	521 (189)	342 (3.1×10^3) [e]		225sh (2.1×10^4)	<200 ($\sim 10^5$)
cis-$[CoL^1(CO_3)][ClO_4]\cdot 1\frac{1}{2}H_2O$	504 (133)	360 (167)		244 (1.8×10^4)	223sh (1.6×10^4) [d]
cis-$[CoL^1(acac)][ClO_4]_2$	494 (131)	368sh		324 (3.7×10^3)	222 (2.1×10^4)
				243sh (1.6×10^4)	

† Band maxima in nm; extinction coefficients (l mol^{-1} cm^{-1}) in parentheses.

[a] Spectra recorded in aqueous solution unless otherwise specified. [b] sh = Shoulder. [c] Measured in 1M-aqueous HCl. [d] Measured in acetonitrile. [e] Assignment uncertain.

Electronic Spectra.—The singlet ground-state nickel

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complex, $[NiL^1][ClO_4]_2$, has a single *d–d* band at 22 420 cm^{-1} (ε 89 l mol^{-1} cm^{-1}) (Table 2). Such a band is characteristic of square planar nickel(II) complexes with four nitrogen donors which normally have a single *d–d* bond near 22 000 cm^{-1} (ε *ca.* 10^2 l mol^{-1} cm^{-1}).[14] The visible spectrum of the analogous copper(II) complex in solution shows a single nearly symmetric band at 19 700 cm^{-1} (ε 87 l mol^{-1} cm^{-1}). The wavelength and intensity of this band is comparable to values reported for copper(II) complexes of related tetra-aza-macrocycles.[19]

The u.v. spectrum of the ligand dihydroperchlorate has a band at 225 nm (ε 370 l mol^{-1} cm^{-1}) which is absent in the reduced macrocycle. This band can therefore be assigned to the $n \rightarrow \pi^*$ transition of the C=N double-bond. In the metal(II) and cobalt(III) complexes this region of the spectrum is complicated by intense charge-transfer transitions, however the zinc(II) complex has a band at *ca.* 240 nm (ε *ca.* 800 l mol^{-1} cm^{-1}) which is probably due to the C=N $n \rightarrow \pi^*$ transition. The cobalt(II) complex does not exhibit any distinct *d–d* bands, although two unresolved shoulders occur on the side of an intense charge-transfer band.

The dihalogeno-complexes of cobalt(III) exhibit three low-intensity absorption bands in the visible region characteristic of the *trans*-$[CoN_4X_2]^{n+}$ chromophore.[20] Such complexes have a basic D_{4h} symmetry, with the $^1A_{1g} \rightarrow {}^1T_{1g}$ (O_h) transition split into two components, $a^1A_{1g} \rightarrow {}^1E_g$ (D_{4h}) and $a^1A_{1g} \rightarrow {}^1A_{2g}$ (D_{4h}) transition.[20,21] Where the tetragonal splitting is not very large as in the *trans*-$[CoN_4L_2]^{n+}$ complexes ($L = NCS^-$, NO_2^-, or NH_3) only a single absorption band is observed under the $^1A_{1g} \rightarrow {}^1T_{1g}$ (O_h) envelope. In the *cis*-compounds the lowest energy transition can be assigned to $^1A_1 \rightarrow ({}^1E + {}^1B_2)$ in C_{2v}. Energies and intensities observed support the assignment of *trans*-structures to the di-anionocompounds and *cis*-structures to the complexes with additional chelating ligands. In all cases the *d–d* bands are at a higher energy for the cobalt(III) derivatives of L^1 than for L^2, indicating a higher ligand-field strength for the dimethyl derivative in both planar and folded co-ordination. The ligand-field strength of L^1 is similar to that of 5,12-dimethyl-7,14-diphenyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene[14,22] in planar co-ordination, and somewhat greater in folded co-ordination. The greater ligand-field strength of L^1 compared with L^2 is probably steric in origin since the hexamethyl derivative has axial methyl substituents.

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