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New Macrocyclic Complexes of Cobalt(II), Nickel(II) and Copper(II)

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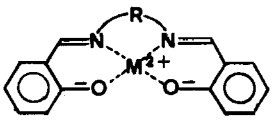
Received May, 12, 1970

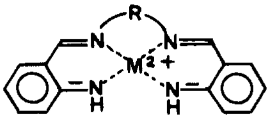
The following complexes have been prepared: 3,4:9,10-dibenzo-1,5,8,12-tetra-aza-cyclotetradecane-1,11-dieneato-nickel(II), -cobalt(II) and -copper(II), (i.e. *XXV, XXIX, and XXXIII*), *3,4:9,10-dibenzo-1,5,8,12-tetra-aza-cyclopentadecane-1,11-dieneato-nickel(II), -cobalt(II) and -copper(II),* (i.e. *XXVI, XXX, XXXIV*), *3,4:9,10-dibenzo-1,5,8,12-tetra-aza-cyclohexadecane-1,11-dieneato-nickel(II), and -cobalt(II),* (i.e. *XXVII and XXXI*)*, 1,5,8,12-tetra-aza-3,4:9,10:13,14-tribenzocyclotetradecane-1,11-dieneato-nickel(II) and -cobalt(II),* (i.e. *XXVIII and XXXII*). *Their physical properties are investigated. The nickel and cobalt compounds are shown to be low spin, tetracoordinate square planar monomers and very reluctant to change their geometry. Various properties of N,N'-ethylenebis-*(o-*amino-benzylideneiminato) copper(II) are described.*

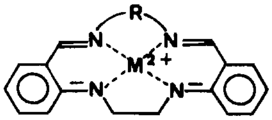
Introduction

Two interesting differences occur between the 'N_2O_2' and 'N_4' type* quadridentate ligands formed by Schiff base condensations of salicylaldehyde and *o*-aminobenzaldehyde respectively with α,ω-diamines, namely the ability to change geometry and coordination number. The parent nickel(II) complexes, N,N'-ethylenebis-(salicylideneiminato)nickel(II), Ni salen(I)[1,2] and N,N'-ethylenebis-(*o*-aminobenzylideneiminato)nickel(II), Ni amben(XIII),[3,4] are both tetracoordinate and square planar in both non-polar and polar solvents. However Ni saltn(II),[2] Ni salbuten(III)[2] and Ni salphen(IV)[1,5] all coordinate with pyridine when dissolved in it, while Ni ambtn(XIV), Ni ambbuten(XV) and Ni ambphen(XVI) remain tetracoordinate and square planar.[3,4] This latter geometry is kept by Co amben(XVII) and Co ambtn(XVIII) under all conditions that have been investigated.[3,6] In contrast Co saltn(VI)[7] adds water as a ligand and also possesses an anomalous structure, not that of a planar, tetracoordinate complex. The next member of the Co salen family, Co salbuten(VII) is tetrahedral.[7] There are probably interactions between Co salen(IX) units in its solid state as its absorption at 877 mμ[8] is not seen in solution.[9]

The Cu salen family is somewhat similar to that of Co salen. In the parent compound there is coordination between the Cu salen(IX) units giving a dimeric structure.[10] Cu salen also coordinates with pyridine when dissolved in it,[11,12] while changes in spectra between Cu salen, Cu saltn(X) and Cu salbuten(XI) suggest increasing tetrahedral distortion.[13,14]







M = Ni,	R = $-(CH_2)_2-$	Ni salen(I)	Ni amben(XIII)	Ni cyen(XXV)
	R = $-(CH_2)_3-$	Ni saltn(II)	Ni ambtn(XIV)	Ni cytn(XXVI)
	R = $-(CH_2)_4-$	Ni salbuten(III)	Ni ambbuten(XV)	Ni cybuten(XXVII)
	R = *o*-phenylene	Ni salphen(IV)	Ni ambphen(XVI)	Ni cyphen(XXVIII)
M = Co,	R = $-(CH_2)_2-$	Co salen(V)	Co amben(XVII)	Co cyen(XXIX)
	R = $-(CH_2)_3-$	Co saltn(VI)	Co ambtn(XVIII)	Co cytn(XXX)
	R = $-(CH_2)_4-$	Co salbuten(VII)	Co ambbuten(XI)	Co cybuten(XXXI)
	R = *o*-phenylene	Co salphen(VIII)	Co ambphen(XX)	Co cyphen(XXXII)
M = Cu,	R = $-(CH_2)_2-$	Cu salen(IX)	Cu amben(XXI)	Cu cyen(XXXIII)
	R = $-(CH_2)_3-$	Cu saltn(X)	Cu ambtn(XXII)	Cu cytn(XXXIV)
	R = $-(CH_2)_4-$	Cu salbuten(XI)	Cu ambbuten(XXIII)	Cu cybuten(XXXV)
	R = *o*-phenylene	Cu salphen(XII)	Cu ambphen(XXIV)	Cu cyphen(XXXVI)

(*) *i.e.* those which coordinate through two nitrogen and two oxygen atoms and those which use four nitrogen atoms.

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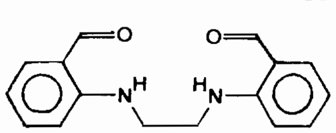
In this Paper, a study is made of the geometry of the nickel(II), cobalt(II) and copper(II) complexes of the 'N_4' cyclic analogues of the amben family. (The trivial prefix cy- is used to refer to these compounds). Co cybuten(XXXI) and Co cyphen(XXXII) are particularly useful for comparison with Co salbuten(VII) and Co salphen(VIII) as they are more readily characterized than Co ambbuten(XIX) and Co ambphen(XX). Various properties of Cu salen are also described here. (A preliminary communication on the cyclic 'N_4' complexes has already been given.[15] A different system was used there for numbering the atoms in the complexes from that in the Abstract here. The present method is more convenient as the four nitrogen atoms now carry the same number irrespective of the compound).

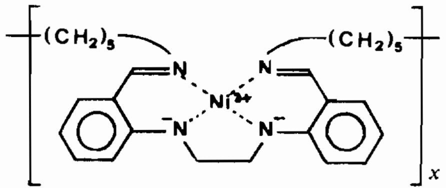
Preparation

The complexes were prepared by refluxing the appropriate diamine with the dialdehyde(XXXVII) in the presence of cobalt(II), nickel(II), or copper(II) acetate in methanol. The cobalt complexes were prepared under nitrogen to prevent formation of possible peroxy-cobalt or cobalt(III) compounds. The mechanism is discussed in the previous paper[16] and the procedure is given in the Experimental Section of this one. An alternative, but less practical, route involved the reaction between preformed ligand and appropriate acetate.



(XXXVII)

The following complexes were obtained and recrystallized: Ni cyen, Ni cytn, Ni cybuten, Ni cyphen, Cu cyen and Cu cytn(XXV) to (XXVIII), (XXXIII) and (XXXIV) respectively. Preparations of Cu cybuten(XXXV) and Cu cyphen(XXXVI) were not attempted. Co cyen, Co cytn, Co cybuten and Co cyphen(XXIX)-(XXXII) were also prepared. These substances are somewhat sensitive to oxygen. (They were probably obtained in a purer state than the data in the Experimental Section indicate, because of slight oxidation during the unavoidable time gap before analysis). Attempts to make a macrocyclic complex with a long bridging group, R, resulted in formation of a what is probably a polymer: when 1,10-diaminodecane is refluxed with the dialdehyde(XXXVII) in methanolic nickel acetate, a dark red amorphous solid is obtained of very low solubility.[16] Its electronic spectrum (in nujol) and its infra-red absorption resemble those of the cyclic nickel complexes above, and like these compounds it is diamagnetic. The compound may be (XXXVIII).



(XXXVIII)

Results

Molecular weight determinations[15] indicate that in benzene Ni cyen(XXV), Co cytn(XXVI) and Cu cyen(XXIX) are monomers.

Infra-red and NMR Spectra. Full details are given in the Experimental Section. The infra-red spectra of corresponding cobalt, nickel and copper complexes are similar, and resemble those of their acyclic cobalt[6] and nickel[4] analogues. Apart from the obvious absence of a signal due to N–H groups, the NMR spectrum of the Ni cyen complexes resemble those of the Ni amben family.[4]

Table I. Magnetic susceptibilities of the solid complexes at room temperature. χ_g and χ_M, mass and molar susceptibilities of the complexes; χ_L, molar susceptibility of ligand from Tables;[17] $\chi_{M'}$, molar corrected susceptibility of metal ion; units, c.g.s.$\times 10^{-6}$. Magnetic moments are calculated over the temperatures indicated assuming a Curie Law

	Temp. (°K)	χ_g	χ_M	χ_L	$\chi_{M'}$	μ
Ni cyen	294	–.250	–87	–175	88	—
Ni cytn	293	.062	21	–187	208	—
Ni cybuten	294	–.181	–68	–199	131	—
Ni cyphen	289	–.506	–201	–186	–15	—
Co cyen	290-291	5.132	1791	–175	1966	2.15 ± .05 B.M.
Co cytn	291-296	4.850	1762	–187	1949	2.15 ± .02
Co cybuten	295-296	6.475	2443	–199	2642	2.51 ± .01
Co cyphen	291-292	5.201	2070	–186	2256	2.30 ± .01
Cu cyen	289-295	3.701	1305	–175	1485	1.86 ± .05
Cu cytn	290-294	3.375	1242	–187	1429	1.85 ± .05

Magnetic Susceptibilities. Susceptibilities obtained using Gouy's Method are given in Table I. The nickel and cobalt complexes are obviously low spin, unlike Co salbuten[7] for example.

Evans' NMR Method[18] was used to study solutions of Ni cytn, Ni cybuten, Cu cytn, Co cytn and Co cybuten in pyridine (the choice of compounds being dictated by solubility). No significant paramagnetism could be detected between 238 and 306°K in the nickel complexes, implying that pyridine is incapable of forming a high spin complex (as it does with Ni salphen[1] for example). Cy cytn was studied in pyridine between 238 and 312°K, over which range the Curie-Weiss Law is obeyed, giving a magnetic moment of 1.82 ± .05 B.M. Cy cytn and Co cybuten were investigated in pyridine over ranges of 238-313°K and 253-313°K respectively. Plots of the reciprocal of corrected molar susceptibility (*i.e.* $\chi_{M'}$ in Table II) against temperature are slightly curved but these deviations from the Curie-Weiss Law are small, and within experimental error. Moments of 2.01 ± .15 B.M. and 2.00 ± .08 B.M. are obtained for Cy cytn and Co cybuten respectively. The value of 2.5 B.M. found for Co cybuten as a solid appears to be significantly greater than that observed in pyridine.

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Table II. Visible spectra of the complexes: λ_{max} (in mμ)(ε)

Ni cyen	560 [a, b]	495(5700) [b]
Ni amben		481(3900)
Ni cytn	620 [a]	520(4470) 480(3900 sh)
Ni ambtn	600 [a]	495(4700), 472(4700)
Ni cybuten	650 [a]	550(3740), 500(3720), 407(4680 sh)
Ni ambbuten	620(800 sh)	515(3600), 475(3700), 470(3700)
Ni cyphen	632(7100)	588(5400), 550(4900 sh), 441(7000 sh)
Ni ambphen	620(7600)	575(5900), 585(5300 sh), 515(5100 sh), 430(9300 sh)
Co cyen	900(110)	640(430 sh), 542(4200), 510(3300 sh), 442(19100)
Co amben	917(57)	530(4450), 431(20200)
Co cytn	930(70)	555(3840), 448(12200)
Co ambtn	960(83 sh)	540(3080), 435(9900)
Co cybuten	940(80)	615(3100 sh), 558(4200), 446(13100)
Co cyphen	950(90) [a, c]	745(1100), [c] 660(2600), [c] 580(4000), 550(8900 sh) 518(3900 sh), 442(15100)
Cu cyen	650(180 sh)	472(3900 sh), 439(13400)
Cu amben	675(203)	460(2100 sh), 422(12000 sh), 415(13000)
Cu cytn	740(150)	490(sh), [a] 439(11000)

Data relate to solutions in dimethylformamide. Similar spectra were obtained in pyridine and nujol except where indicated. [a] In nujol, [b] in benzene 565(2590 sh), 510(5300) and 482(4550 sh), [c] in dimethylsulphoxide.

Electronic Spectra. The spectra of the cyen complexes are similar to those of the corresponding amben[3,4,6] systems. The positions and intensities of maxima in the visible region are given in Table 2. The corresponding free ligands[4] are colourless (although they absorb in the ultra-violet, just as the complexes do). It seems very probable therefore that the more intense visible absorptions are due to metal→ligand transitions as in Ni salen.[19]

In some of the Ni amben complexes, broad, rather less intense transitions can be seen at about 600 mμ, with ε 800, which we[4] consider to be d–d. In the cyclic complexes, shoulders can be seen at slightly longer wavelengths, when samples are run in benzene or as nujol mulls. If these are d–d transitions, and if their frequency is directly related to field strength, then the cyclic ligands must exert ligand fields very similar to the acyclic analogues. The sequence for Ni cyen, Ni cytn and Ni cybuten of 560 mμ, 620 mμ and 650 mμ is compatible with the fall in ligand field that would be expected from increase in the length of R. No absorption occurs in the very near infra-red region up to 1000 mμ.

The weak absorption bands of the Co cyen compounds between 900 and 1000 mμ resemble those of the Co amben analogues and are presumably d–d transitions. In this series of complexes there is no sign of any distortion to a tetrahedral high spin state such as occurs in Co salbuten,[7] in spite of the fact that Co cybuten is rather strained in a planar configuration. The bands around 700 mμ are presumably also d–d. In both the cobalt and copper compounds the energy of these transitions falls as the length of the bridging group, R, increases, which as in the case of the nickel compounds can be accounted for in terms of decreasing ligand field.

No appreciable changes in the electronic spectra are shown by either the nickel, the cobalt or the copper 'N_4' complexes between media, such as pyridine, dimethylformamide and nujol for example. Although there are small differences, they are not of the magnitude of those seen in Ni salphen[2] and Cu salen[11,12] between chloroform and pyridine, Co saltn between water and the solid phase,[7] or Cu salen between chloroform[9] and the solid.[8] Minor distortions may be responsible for the small differences.

Discussion

Ni cyen and Co cytn are both monomers in benzene. Conjugation would be expected to impose a planar structure on the ligands in Ni cyphen and Co cyphen, in particular on the four nitrogen atoms. Therefore all the nickel and cobalt complexes probably possess structures that are monomeric and square planar (or nearly so), as members of the same family have very similar electronic spectra. (There are pronounced differences in the spectra of Co salen, Co saltn and Co salbuten,[7] which have different geometries as was mentioned in the Introduction). The lack of any major alterations in spectra between nujol, dimethylformamide and pyridine points to an absence of both weakly coordinated ligands in the axial positions, and appreciable interactions in the solid phase between monomer units. The diamagnetism of the nickel complexes is compatible with this picture. Moments in the ranges 2.2-2.9 B.M., 1.89-2.36 B.M. and 1.70-1.85 B.M. are observed for tetra-, penta- and hexa-coordinate low spin[20] cobalt(II) complexes. The values observed for Co cyen and Co cytn thus lie right at the bottom end of the tetracoordinate range but in the middle of the pentacoordinate one, while the moment of Co cybuten decreases on solution in pyridine, However there is no spectroscopic evidence to suggest any labile ligands analogous to that seen when Co saltn adds water.[7] It seems reasonably fair to state therefore that the nickel and cobalt cyclic 'N_4' complexes studied here are low-spin, tetracoordinate monomers, which are square planar (or nearly so), and possess a strong tendency to keep these properties. The same is true of the acylic 'N_4' complexes, Ni amben, Ni ambtn, Ni ambbuten, Ni ambphen, Co amben and Co ambtn.[3,4,6]

As Cu cyen is monomeric in benzene, and as the electronic spectra of it, Cu amben and Cy cytn are very similar and not altered by change in medium, all three are probably monomeric and tetracoordinate.

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(Cu salen and Cu salpn (IX, but with $R = -CH_2CH(CH_3)-$) have different colours in chloroform and pyridine,[11] while Cu salen, Cu saltn and Cu salbuten have rather different spectra as solids[13] and dissolved in pyridine[21]). Unfortunately it is not easy to choose between a square planar and a tetrahedral geometry. The magnetic moments in the range 1.8-2.1 B.M. found for Cu cyen and Cu cytn (and also observed[14] for Cu salen, Cu saltn and Cu salbuten) are compatible with either geometry.[14,20] (Incidentally they are too high however for there to be any Cu—Cu interaction[20]). However in Cu amben and Cu cyen a planar configuration would be much less strained than a tetrahedral one. Moreover Cu salen[10] and Cu salpn[22] (IX, but with $R = -CH_2CH(CH_3)-$), though showing pentacoordination, have nearly planar CuN_2O_2 groups. Therefore it will be assumed that Cu amben and Cu cyen are essentially square planar. As no spin change accompanies the distortion of a square planar d^9 complex to a tetrahedral shape, it is much more difficult to use electronic spectra to compare geometires than in the d^7 and d^8 cases. The d–d transitions move to higher wavelengths in the sequence, Cu salen, Cu saltn, Cu salbuten, but this could be due to a fall in ligand field strength in a planar complex as R becomes longer[21] or to increasing tetrahedral distortion[13] (which seems more likely). Either explanation is compatible with the movement of d–d bands from 650 mμ to 740 mμ between Cu cyen and Cu cytn. There would be a certain neatness if the ' N_4 ' ligands, cytn, cybuten, were able to retain planar structure in their copper complex just as they do in their cobalt compounds (in spite of steric strain) but there is no evidence on this point.

The ability of the acyclic ' N_4 ' nickel and cobalt complexes to resist both tetrahedral distortion and addition of further ligands was discussed earlier in terms of ligand field strengths.[3,4,6] The members of the amben family were considered to exert higher ligand fields than their salen counterparts. If that argument is correct, then the cyen ligands must also exert large ligand fields.

Experimental Section

Ni cyen(XXV) was prepared by adding to a stirred suspension of 4,7-diaza-2,3: 8,9-dibenzodecane-1,10-dione(XXXVII) (0.73 g, 2.7 mmole) in refluxing methanol (20 ml) nickel(II) acetate (0.68 g, 2.7 mmole), followed by 1,2-diaminoethane (0.36 ml, 5.5 mmole) in methanol (10 ml). After six hours the mixture was filtered, and the infrared spectrum of the fine purple-red needles showed the absence of 4,7-diaza-2,3: 8,9-dibenzodecane-1,10-dione. Recrystallization of this product from a mixture (3: 1) of benzene and petrol (80-100°) (c.a. 150 ml) gave Ni cyen (.41 g 45%) as fine purple needles. Found C, 61.78; H, 5.37; N, 15.46; $C_{18}H_{18}N_4Ni$ requires C, 61.93; H, 5.19; N, 16.05. Molecular weight in benzene by so-called osmometry, 362; formula above requires, 349. τ(chloroform-d) 2.40 (methine, singlet); 2.8-3.9 (aromatics, complex); 6.56 («imino» methylene, singlet); 6.69 («anilino» methylene, singlet). ν(nujol and hexachlorobutadiene): 3075w, 3055w, 3020w, 3005w, 2945sh, 2935w, 2917w, 2895m, 2865sh, 2855m, 2832sh, 1613s, 1603sh, 1564m, 1555sh, 1525s, 1518s, 1482s, 1455s, 1442s, 1931m, 1364m, 1358m, 1350m, 1344m, 1270w, 1235w, 1218s, 1203s cm^{-1}. The same procedure as for Ni cyen gave similar yields of Ni cytn, Ni cybuten, Cu cyen and Cu cytn.

Ni cytn(XXXVI). Found C, 62.62; H, 5.71; N, 15.58; $C_{19}H_{20}N_4Ni$ requires C, 62.84; H, 5.55; N, 15.43. τ(chloroform-d) 2.65 (methine, singlet); 2.8-3.9 (aromatics, complex); 6.38 («imino» α-methylene, triplet, $J=7$ c./sec) 6.84 («anilino» methylene, singlet), 8.08 («imino» β-methylene, quintet, $J=7$ c/sec). ν-(nujol): 3065w, 3050w, 3045w, 3015w, 2820m, 2815m, 1614s, 1540sh, 1529s, 1520sh, 1470s, 1391m, 1376s, 1370sh, 1358s, 1348m, 1268w, 1226m, 1218m, 1210s cm^{-1}.

Ni cybuten(XXVII). Found C, 63.19; H, 6.15; N, 14.55; $C_{20}H_{22}N_4Ni$ requires C, 63.69; H, 5.88; N, 14.86. τ(chloroform-d) 2.66 (methine, singlet), 2.8-3.8 (aromatics, complex), 6.38 («imino» α-methylene, broad), 6.90 («anilino» methylene, singlet), 8.30 («imino» β-methylene, broad). ν(nujol): 3060w, 3045w, 3040w, 1608s, 1584m, 1528s, 1520sh, 1515sh, 1470s, 1461sh, 1435sh, 1395w, 1385sh, 1375m, 1349m, 1324m, 1305w, 1265m, 1240w, 1222m, 1212m cm^{-1}.

Cu cyen(XXXIII). Found C, 60.00; H, 5.45; N, 15.44; $C_{18}H_{18}N_4Cu$ requires C, 61.08; N, 5.13; H, 15.83. ν(nujol and hexachlorobutadiene): 3076w, 3055w, 3020w, 3010w, 2943w, 2920w, 2899m, 2864m, 2850m, 2822m, 2790m, 1614s, 1598sh, 1565m, 1555sh, 1525s, 1518s, 1479s, 1456s, 1545s, 1440s, 1430sh, 1400w, 1389s, 1373w, 1362m, 1351m, 1341w, 1265w, 1260w, 1238w, 1210sh cm^{-1}.

Cu amben(XXI). The complex was prepared using the method of Pfeiffer[23] and his group, and recrystallized from dimethylformamide. ν(nujol): 3308w, 3080w, 3059w, 3018w, 2950s, sh, 2918s, 2853s, 1603s, 1559s, 1522s, 1475sh, 1437s, 1417sh, 1374m, 1320s, 1300m, 1329m, 1322sh, 1222m cm^{-1}.

Cu cytn(XXXIV). Found C, 62.56; H, 5.76; N, 15.45; $C_{19}H_{20}N_4Ni$ requires C, 62.02; H, 5.48; N, 15.22. ν(nujol): 3062(w), 3040w, 3020w, 2815m, 1612s, 1590sh, 1540sh, 1531m, 1476s, 1465s, 1445sh, 1435sh, 1399w, 1390sh, 1375s, 1365sh, 1350sh, 1260w, 1210s, b cm^{-1}.

Ni cyphen(XXVIII) was prepared by adding to a stirred suspension of 4,7-diaza-2,3: 8,9-dibenzodecane-1,10-dione (0.53 g, 2.0 mmole) in a methanolic (50 ml) solution of nickel(II) acetate (0.52 g, 2.1 mmole) refluxing under nitrogen, a solution of 1,2-diaminobenzene (0.64 g, 5.9 mmole) in methanol (10 ml). After refluxing for 6 hr the almost black mixture was sampled, and the solid found, from its infrared spectrum, to contain some of the starting dialdehyde. After 24 hr no dialdehyde could be detected, and the mixture was filtered, and the mass of dark needles recrystallized from benzene by slow evaporation of the solution (*ca.* 100 ml) under a stream of nitrogen, when Ni cyphen (0.46 g, 58%), was obtained as deep blue-green fine needles. Found C, 66.43; H, 4.59; N,

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14.14; $C_{22}H_{18}N_4Ni$ requires C, 66.54; H, 4.57; N, 14.10. ν(nujol): 3082w, 3062w, 3050w, 3042w, 3012w, 2962sh, 2945sh, 2922m, 2885m, 2845m, 2815sh, 1609s, 1571s, 1534sh, 1514s, 1510s, 1470s, 1452s, 1442m, 1430s, 1390s, 1371s, 1355s, 1348sh, 1330sh, 1267m, 1242w cm^{-1}.

Co cyen(XXIX) was prepared in the following way. A suspension of 4,7-diaza-2,3:8,9-dibenzodecane-1,10-dione (1.2 g, 4.5 mmole) in methanol (60 ml) was refluxed gently under a slow stream of nitrogen. The mixture was stirred vigorously and cobalt(II) acetate (1.2 g, 4.8 mmole) was added, followed by a solution of 1,2-diaminoethane (0.64 ml, 9.6 mmole) in methanol (10 ml). After two hours the matted crystals were broken into smaller lumps to reduce the violent bumping. After six hours the mixture was filtered under nitrogen, and the residue washed with a little methanol, when Co cyen was obtained as fine purple needles which were allowed to dry on the sinter by passing a slow stream of nitrogen over them (1.4 g 86%). (These crystals could not be recrystallized from any of a wide range of solvents tested). Found: C, 61.24; H, 5.35; N, 15.77; $C_{18}H_{18}N_4Co$ requires C, 61.89; H, 5.19; N, 16.03. ν(nujol and hexachlorobutadiene): 3060w, 3050w, 3025w, 3005w, 2980sh, 2960sh, 2945w, 2940m, 2905w, 2880w, 2865m, 1602s, 1585m, 1572sh, 1565sh, 1523s, 1517sh, 1490sh, 1479w, 1438s, 1427s, 1398w, 1373m, 1338s, 1326m, 1266m, 1244w, 1230sh, 1215s cm^{-1}.

The same procedure was used for the preparation of Co cytn and Co cybuten.

Co cytn(XXX). Found: C, 62.55; H, 5.58; N, 15.47; $C_{19}H_{20}N_4Co$ requires C, 62.81; H, 5.55; N, 15.42. Molecular weight in benzene by so-called osmometry 402; formula above requires 363. ν(KBr): 3080w, 3060w, 3050w, 3010w, 2980w, 2945w, 2935w, 2920m, 2860m, 2820m, 1603s, 1580s, 1572sh, 1525s, 1520sh, 1515sh, 1505sh, 1475s, 1450sh, 1439sh, 1429s, 1395sh, 1385w, 1370sh, 1350s, 1335sh, 1325sh, 1292w, 1263m, 1222sh, 1215s cm^{-1}.

Co cybuten (XXXI). Found C, 62.95; H, 5.94; N, 14.12; $C_{20}H_{22}N_4Co$ requires C, 63.66; H, 5.87; N, 14.85. ν(nujol): 3060w, 3040w, 3015w, 1602s, 1578s, 1527s, 1523s, 1520sh, 1470s, 1460sh, 1440sh, 1430s, 1377s, 1367m, 1346s, 1330sh, 1310w, 1279w, 1259w, 1222s, 1215sh cm^{-1}.

Co cyphen (XXXII). was prepared by the same method as Ni cyphen, a similar yield being obtained. All attempts at recrystallization failed. Found C, 65.68; H, 4.49; N, 14.45; $C_{22}H_{18}N_4Co$ requires C, 66.50; H, 4.47; N, 14.10. ν(nujol): 3080w, 3050w, 3035w, 3020w, 1608s, 1597sh, 1570s, 1565s, 1520s, 1495w, 1485w, 1465s, 1455sh, 1439sh, 1379s, 1362s, 1348m, 1252w, 1247m, 1212w cm^{-1}.

Analyses were performed by Dr. A. Bernhardt of Mülheim. Infra-red spectra were recorded on a Unicam SP200G, and electronic spectra on a Cary 14. NMR spectra were carried out by Mrs. M. Sutherland on a Perkin-Elmer R10 instrument, chemical shifts being quoted relative to tetramethylsilane.

Acknowledgments. Our thanks to Dr. J. Smith for advice on measurement of magnetic susceptibilities and to Mrs. Sutherland. P.A.T. acknowledges with gratitude a research studentship from the Science Research Council of the United Kingdom.