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Coordination Compounds of Benzildihydrazone

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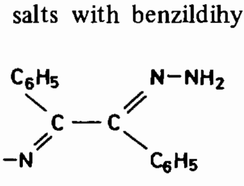
Abstract

New complexes of the general formulae $MCl_2(BZDH)$ (M = Fe, Co), $CoCl_2(BZDH)_2$, $MX_2(BZDH)_2$ (M = Co, Ni and X = Br, I, NCS, NO_3) and $CdI_2(BZDH)$, where BZDH is benzildihydrazone, have been prepared and characterised by elemental analyses, magnetic moments and spectral (IR and diffuse reflectance electronic) studies. The iron(II), cobalt(II) and nickel(II) complexes have high-spin octahedral stereochemistries and are probably polymeric, with bidentate N-methine coordination of the ligand. The correlation of the presence of the phenyl groups in the ligand with the preparative conditions and the stoichiometries of the complexes is also discussed.

Introduction

Ligands with N–N bonds have been much studied in recent years because of their relationship to the problem of conversion of dinitrogen to ammonia or hydrazine and the reaction of coordinated nitrogen. The interest in the study of hydrazones has been growing due to their use in biological systems [1] and analytical chemistry [2]. Ligands containing the –N=C–C=N– grouping are amongst the best known chelating agents *e.g.* dimethylglyoxime, 2,2′-bipyridine and 1,10-phenanthroline. Other ligands containing this grouping can be synthesised by condensation reactions between 1,2-diketones and hydrazines.

As part of our systematic investigation of the coordination chemistry of α-dihydrazone ligands [3–6], we report here the preparation and study of complexes of iron(II), cobalt(II), nickel(II) and cadmium(II) salts with benzildihydrazone (I, BZDH). Fisher and Stoufer [7] were the first to prepare $[Co(BZDH)_3]Cl_2$ and $[Ni(BZDH)_2Cl_2]$ during an investigation of intraligand steric hindrance in α-dihydrazone complexes. Later Renk and Dieck [8, 9] characterised (BZDH)phosphinemolybdenum(0) tricarbonyl and (BZDH)bis(phosphine)molybdenum(0) dicarbonyl and obtained precise information about the oxidation state of the metal, the direction of the low energy electronic transition and the importance of π-back bonding. Very recently we attempted to prepare benzilbis(N,N-dimethylhydrazone), but we unexpectedly obtained 1-methyl-3,4-diphenylpyrazole; complexes of this heavily substituted pyrazole have been prepared and studied [10].



(I, BZDH)

Experimental

Experimental techniques were as described previously [3]. Benzildihydrazone was prepared by the method described by Cope, Smith and Cotter [11]; it was recrystallised from absolute ethanol. M.p. 147–149 °C (lit. 150–1 °C) *Anal.* Found: C, 70.32; H, 5.87; N, 23.57%; $C_{14}H_{14}N_4$ requires C, 70.55; H, 5.93] N, 23.51%. The ^1H NMR ($CDCl_3$) spectrum of BZDH shows a complex of peaks at δ 8.11, 8.03, 8.01, 7.97, 7.92, 7.82, 7.76, 7.70 and 7.65 ppm downfield from TMS assigned to the C_6H_5–protons and a broad singlet at δ 6.07 ppm assigned to the $-NH_2$ protons; the integrations of the signals were in the ratio 10:4.

Preparation of the Complexes

Two general methods of preparation of complexes of BZDH were used. The first method involved the direct reaction of an ethanolic (refluxing methanolic in the case of nickel(II) thiocyanate) solution of the metal salt with a hot ethanolic or ethanolic–ethereal solution of BZDH. In the second method, the anhydrous metal salt was heated under reflux in absolute ethanol with benzil and hydrazine monohydrate (*i.e.* template synthesis); in these preparations the benzil had to be kept in > 1:2 molar ratio with the hydrazine or else the product was contaminated with a quantity of the hydrazine complex of the metal ion. The second method did not work well if hydrated

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metal salts were used as starting materials; the products were often contaminated with metal hydroxides. The iron(II) and cobalt(II) complexes were prepared under an atmosphere of dry nitrogen. In most cases the reaction mixtures were filtered hot and the precipitates were washed with boiling ethanol and ether. The complexes were dried *in vacuo* over silica gel. Efforts to prepare complexes with other stoichiometries (*i.e.* 1:3, 1:2 with iron(II) chloride and cadmium(II) iodide, 1:1 with cobalt(II) bromide, iodide, thiocyanate and nitrate, nickel(II) salts and iron(II) bromide), using various metal ion: ligand molar ratios and different reflux times, met with failure. In some cases products with poor analytical results (contaminated with free BZDH) were obtained. No complexes of BZDH with manganese(II), zinc(II) and mercury(II) salts could be prepared. When copper(II) salts in hot ethanolic solutions were treated with the ligand, the resulting reactions were very complicated; effervescence occurred and yellow or off-white precipitates were deposited. The products were diamagnetic suggesting reduction of copper(II) to copper(I). The analyses and the IR spectra of these solids indicated that some decomposition of the free ligand had occurred.

Representative examples of preparations are described below.

Dinitratobis(benzildihydrazone)nickel(II), $Ni(NO_3)_2(BZDH)_2$

A solution of nickel(II) nitrate hexahydrate (1.45 g, 0.005 mol) in 25 ml of warm absolute ethanol and 5.5 ml of triethyl orthoformate (dehydrating agent) was added slowly with constant stirring to a refluxing solution of BZDH (3.57 g, 0.015 mol) in 65 ml of absolute ethanol and 65 ml of ether. A green product formed immediately. The reaction mixture was filtered warm and washed with boiling ethanol (3 X 5 ml) and ether (3 X 10 ml) to yield 3.3 g of the finely-divided complex. The same compound was isolated when 2.38 g (0.010 mol) of BZDH were used for the preparation.

Using hydrated nickel(II) iodide, nickel(II) thiocyanate, cobalt(II) iodide, cobalt(II) nitrate and anhydrous iron(II) bromide as starting materials, the above synthetic procedure gave bis-ligand complexes.

Dichlorobis- and Mono(benzildihydrazone)cobalt(II), $CoCl_2(BZDH)_2$ *and* $CoCl_2(BZDH)$

When cobalt(II) chloride (hydrated or anhydrous) was used as starting material, two complexes were isolated. The first was prepared by treating cobalt(II) chloride (0.010 mol) in hot ethanolic solution (20 ml) with BZDH (4.77 g, 0.020 mol) also in hot ethanolic solution (90 ml). The resulting solution was then heated gently for 10 min; a pale brown solid was precipitated upon cooling to room temperature. The product was filtered off and washed and dried as described above; this compound was the bis-ligand complex. The 1:1 adduct was prepared by heating a similar starting mixture for 2 h under reflux in a nitrogen atmosphere. The product was precipitated as a pink solid from the hot ethanolic solution. The mixture was filtered hot and washed and dried as before.

With cadmium(II) iodide and iron(II) chloride, procedures similar to the second of the two cobalt(II) chloride preparations yielded $CdI_2(BZDH)$ and $FeCl_2(BZDH)$, respectively. The cobalt(II) thiocyanate complex was precipitated after only 5 min refluxing.

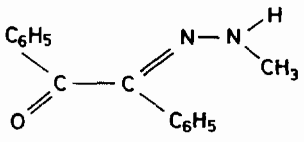
Dibromobis(benzildihydrazone)cobalt(II), $CoBr_2(BZDH)_2$ *(Template Synthesis)*

Anhydrous cobalt(II) bromide (2.19 g, 0.010 mol) was heated under reflux in ethanolic solution with benzil (4.62 g, 0.022 mol) and hydrazine monohydrate (2 ml, 0.041 mol) for 4 h and the resulting solution was allowed to cool to room temperature. Cream to pale brown coloured microcrystals were deposited. These were filtered off, washed and dried as usual.

Template synthesis exactly analogous to that used with cobalt(II) bromide yielded $NiBr_2(BZDH)_2$, when anhydrous nickel(II) bromide was used as a starting material.

Other Synthetic Procedures

We were also interested in studying the coordination chemistry of benzilbis(methylhydrazone), but we could not prepare this ligand. In an attempted preparation, a solution of benzil (21.0 g, 0.10 mol) in absolute ethanol (220 ml) was treated with methylhydrazine (17.5 ml, 0.30 mol). The resulting mixture was heated under reflux for 12 h in a nitrogen atmosphere. The hot solution was allowed to cool to room temperature, when yellow crystals were formed. The mixture was filtered and the crystals were washed with ether and dried *in vacuo*. More product was obtained by distilling away all the ethanol and recrystallising the residue. The ^{1}H-NMR ($CDCl_3$) spectrum of the product shows a complex of peaks between δ 8.71–7.80 ppm downfield from TMS due to C_6H_5–protons, a broad peak at δ 7.05–6.98 ppm and a doublet at δ 3.83 and 3.76 ppm; the integrations of these signals were in the ratio 10:1:3. The spectrum suggests that the solid is benzilmono(methylhydrazone) (**II** BZMMH), the doublet being



(II, BZMMH)

TABLE I. Colours and Analytical Data for Complexes of Benzildihydrazone. Elemental Analyses[a] (%).

Complex	Colour	C	H	N
$FeCl_2(BZDH)$	rust	46.9 (46.1)	3.77 (3.87)	15.5 (15.4)
$FeBr_2(BZDH)_2$	pale yellow	48.6 (48.6)	4.12 (4.08)	16.0 (16.2)
$CoCl_2(BZDH)_2$	pale brown	55.4 (55.4)	4.78 (4.66)	18.7 (18.5)
$CoCl_2(BZDH)$	pink	44.5 (45.7)	3.78 (3.84)	15.0 (15.2)
$CoBr_2(BZDH)_2$	cream-pale brown	48.2 (48.4)	4.15 (4.07)	16.0 (16.1)
$CoI_2(BZDH)_2$	khaki-pale brown	43.1 (42.6)	3.56 (3.58)	14.1 (14.2)
$Co(NCS)_2(BZDH)_2$	yellow-pale brown	54.0 (55.3)	4.37 (4.34)	20.8 (21.5)
$Co(NO_3)_2(BZDH)_2$	pale orange	50.9 (51.0)	4.57 (4.29)	21.1 (21.2)
$NiBr_2(BZDH)_2$	green	48.0 (48.4)	3.99 (4.07)	15.6 (16.1)
$NiI_2(BZDH)_2$	light green	42.6 (42.6)	3.56 (3.58)	14.0 (14.2)
$Ni(NCS)_2(BZDH)_2$	yellow green	55.3 (55.3)	4.34 (4.34)	20.9 (21.5)
$Ni(NO_3)_2(BZDH)_2$	green	50.3 (51.0)	4.31 (4.29)	20.8 (21.2)
$CdI_2(BZDH)$	white	27.5 (27.8)	2.35 (2.34)	9.0 (9.3)

[a] Theoretical values in parentheses.

due to the CH_3- protons and the broad peak to the amino proton. The IR (Nujol) spectrum shows a very strong and broad band at 1685 cm^{-1} assigned to $\nu(C=O)$. *Anal.* Found: C, 75.2; H, 5.93; N, 11.8%; $C_{15}H_{14}N_2O$ requires C, 75.6; H, 5.93; N, 11.8%. The reaction was repeated with longer reflux times, this however led to decomposition of the product. Catalysis with acetic acid and also with mineral acids did not produce a dihydrazone or a pyrazole [10]. When propan-1-ol was used as a solvent the product was again the monohydrazone. Attempts to isolate complexes of BZMMH failed.

Other attempts to prepare complexes of benzilbis-(methylhydrazone) by template syntheses were also carried out. The products, however, were complexes of methylhydrazine.

Results and Discussion

The prepared complexes are listed in Table I with their colours and elemental analyses. The dihydrazones derived from diacetyl, studied previously [4, 6], form complexes immediately upon reaction with metal salts. BZDH forms complexes much less readily; in some cases the reaction mixtures must be heated under reflux for 2–4 h before a complex can be isolated. Zinc(II) salts which react readily with hydrazones of diacetyl do not form complexes with BZDH. The complexes are microcrystalline or powder-like and stable in atmospheric conditions; the two iron(II) complexes isolated are quite stable to aerial oxidation so that BZDH is capable of stabilising iron(II) with respect to oxidation in the way that 1,10-phenanthroline and diacetyldihydrazone do. The complexes listed are insoluble in organic solvents, such as chloroform and nitromethane, so that measurements of molar conductivity and electronic spectra in solutions have been precluded.

The principal infrared bands of interest are listed in Table II. The two strong bands which occur at 3338 and 3180 cm^{-1} are attributed to the antisymmetric and symmetric NH_2 stretching vibrations [12]. The frequencies of these bands are somewhat lower than those ususally associated with these vibrations (3500 to 3250 cm^{-1}); this is due to the interaction between the nitrogen atom of the NH_2 group and the imine nitrogen, both of which have electron pairs with p symmetry [13]. The absence of large systematic shifts of the $\nu_{as}(NH_2)$, $\nu_s(NH_2)$ and $\delta(NH_2)$ bands in the spectra of the complexes implies that there is no interaction between the amino groups and the metal ions. The relatively small shift of the $\nu(NH_2)$ modes to lower frequencies and the rather broad character of these bands is expected to arise from hydrogen bonding to the NH_2 protons with the bonded anions, but any reductions in $\nu(NH_2)$ are not as large as expected if coordination had occurred.

The significant changes in the ligand bands upon complexing are the increases in $\nu(C=N)$ and $\nu(N-N)$. We assign the band at 1549 cm^{-1} in BZDH to $\nu(C=N)$; this disagrees with the assignment made by Fisher and Stoufer [7] at 1582 cm^{-1}. The spectrum of diacetyldihydrazone exhibits the $\nu(C=N)$ mode at 1568 cm^{-1} [6]. Since it has been shown that aromatic substituents tend to produce a reduction in $\nu(C=N)$ [12] and since there are no other bands between 1545 and 1485 cm^{-1}, our assignment seems to be certain. The low energy position of this absorption has been attributed to the existence of an extended π-electron system in a *trans* planar conformation [7, 13]; this conformation does not cause any steric interaction between the well-separated phenyl groups. The movement of this band

TABLE II. Diagnostic Infrared Bands (cm^{-1}) of Benzildihydrazone and its Complexes.

Compound	Ligand Bands					Anion Bands						Far-IR Bands
	$\nu_{as}(NH_2)$	$\nu_s(NH_2)$	$\delta_s(NH_2)$	$\nu(C=N)$	$\nu(N-N)$	$\nu(CN)$	$\nu(CS)$	$\delta(NCS)$	$\nu_{as}(NO_2)$	$\nu_s(NO_2)$	$\nu_6(B_1)$[b]	
BZDH	3338, 3259	3180	1614	1549	1097							318[c], 301[c], 272[c]
$FeCl_2(BZDH)$	3355, 3265	3178	1610	1524	1131							290, 245
$FeBr_2(BZDH)_2$	3265	3138	1612	1556	1138							281
$CoCl_2(BZDH)_2$	3380	3195	1611	1569	1122							291, 233
$CoCl_2(BZDH)$	3264, 3240	3130	1612	1570	1134							283
$CoBr_2(BZDH)_2$	3258	3125	1611	1569	1119							289, 276sh
$CoI_2(BZDH)_2$	3252	3122	1610	1562	1123							290, 276
$Co(NCS)_2(BZDH)_2$	3270	3135	1616	[a]	1125sh	2080	805	470				284sh, 271, 218
$Co(NO_3)_2(BZDH)_2$	3300	3142	1618	1559sh	1131				1448	1302	813	298, 278, 229
$NiBr_2(BZDH)_2$	3244	3115	1608	1563	1129							296, 241
$NiI_2(BZDH)_2$	3240	3125	1610	1559	1124							298, 275sh
$Ni(NCS)_2(BZDH)_2$	3262	3132	1618	1562sh	1130	2098	796	468				290, 274, 225
$Ni(NO_3)_2(BZDH)_2$	3290	3141	1618	1565	1133				1450	1300	811	302, 278
$CdI_2(BZDH)$	3279	3181	1617	1572	1139							269

[a] Not observed. [b] Out-of-plane rocking in C_{2v}. [c] These bands are very weak; sh = shoulder.

to higher frequencies in the spectra of the complexes is as has been observed in alkyl cyanide complexes [14] and in complexes of other ligands containing the >C=N–N< grouping [3–6, 7, 13], in which the imino nitrogen atom donates to the metal ion. As the tendency for metal electrons to be delocalized toward the BZDH molecules increases by interaction of the π symmetry metal orbitals with those ligand orbitals of the appropriate symmetry, the C=N bond order will decrease accordingly. Thus, the greater the extent of π bonding between the metal atom and ligand molecules, the lower will be the frequency position of the C=N stretching vibration. Consideration of the spectra shows that ν(C=N) of iron(II) complexes <ν(C=N) of cobalt(II) and nickel(II) complexes; this is in accordance with the general accepted order of decrease of metal–ligand π bonding which is $Fe^{II} > Co^{II} \simeq Ni^{II}$. In $FeCl_2(BZDH)$ this absorption is found at a lower frequency compared with that of the free ligand. Fisher and Stoufer [7] made no assignment of ν(N–N) for BZDH. We assign the band at 1097 cm^{-1} to ν(N–N) in accord with the assignments of this band in N–N bonded molecules [3–6, 15]. Shift of ν(N–N) to higher frequencies has been observed in hydrazine [15] and other α-dihydrazone [3, 6] complexes.

The IR spectrum of $Co(NCS)_2(BZDH)_2$ exhibits ν(CN), ν(CS) and δ(NCS) modes in the regions characteristic of terminal N-bonded isothiocyanate groups [16]. The nickel(II) analogue has a ν(CN) band at 2098 cm^{-1}; this is a frequency common to N-bonded thiocyanates (usually found at *ca.* 2050–2100 cm^{-1}) and bridging thiocyanates (usually found at *ca.* 2090–2140 cm^{-1} [16]. The ν(CS) band has been identified as 796 cm^{-1} and it is in the region for N-bonded thiocyanates [16]; this band is probably too high in frequency for bridging thiocyanates, since these normally produce a band only moderately higher than the free ion value of *ca.* 750 cm^{-1}; many bridged complexes have ν(CS) at *ca.* 780 cm^{-1} [17]. N-bonded thiocyanates are, therefore, most likely for $Ni(NCS)_2(BZDH)_2$. The absence of a band in the 1350–1400 cm^{-1} region in the spectra of the nitrate complexes confirms that ionic nitrates are absent [18]. The values of the frequencies assigned as vibrational modes of the nitrate group in Table II are strongly indicative of the presence of coordination monodentate nitrates [19, 20]. The separation of the two highest frequency bands is *ca.* 150 cm^{-1}; for bidentate nitrates this separation is larger than 185 cm^{-1}. The $\nu_2(A_1)$, $\nu_3(A_1)$ and $\nu_4(B_2)$ modes of the C_{2v} nitrato groups [19, 20] were not assigned, because the regions at *ca.* 1000 and 700–760 cm^{-1} are obscured by strong bands of coordinated BZDH. The 1700–1800 cm^{-1} region is viewed as the key to differentiate with certainty between bidentate and unidentate coordination [20]. The separation of the combination bands appearing around 1755 and 1735 cm^{-1}, is about 20 cm^{-1} and this fact indicates monodentate nitrato groups [18, 20].

The region of the free ligand's spectrum between 350 and 215 cm^{-1} contains only three very weak bands. This would indicate that some of the other bands observed in this region would be assignable to ν(M–N) [21] and ν(M–X) [19, 20] vibrations. A comparison, however, of the Far-IR spectra between BZDH and its metal complexes fails to give clearcut assignments. A very strong band at 233 cm^{-1} in the spectrum of $CoCl_2(BZDH)_2$ probably arises from the $\nu(Co–Cl)_t$ vibration in a *trans* (D_{4h}) structure [22].

Table III gives the room temperature magnetic moments and details of the diffuse reflectance electronic spectra of the complexes. The μ_{eff} values of the chloride and bromide iron(II) complexes are 5.37 and 5.28 BM respectively, indicating high-spin complexes. Both complexes have electronic spectra consistent with six-coordinate structures [23, 24]. In the case of $FeBr_2(BZDH)_2$ the d–d band is clearly split into two components which represent transitions to the ^5E_g state whose degeneracy has been lifted by the Jahn–Teller effect. The spectra also exhibit relatively low-energy charge-transfer bands predominantly of the metal to ligand class [24].

The μ_{eff} values of the cobalt(II) complexes lie in the 4.94–5.23 range, characteristic of octahedral stereochemistry. Their electronic spectra exhibit bands typical of octahedral symmetry [24]. The 10 Dq values for the bis-ligand complexes are lower than that found in $[Co(BZDH)_3]Cl_2$ [7], as expected from the high position of this ligand in the spectrochemical series. The mono-ligand chloride complex is in a two-nitrogen, four-chloride environment.

The μ_{eff} of the nickel(II) complexes show only small orbital contribution, in accord with octahedral stereochemistry. The electronic spectra exhibit the three well-defined transitions between the triplet states in this geometry, with some evidence of tetragonal distortion in $Ni(NCS)_2(BZDH)_2$ [24]. As the symmetry is lowered to D_{4h}, the $^3A_{2g} \rightarrow {}^3T_{2g}$ transition is split into $^3B_{1g} \rightarrow {}^3B_{2g}$ and $^3B_{1g} \rightarrow {}^3E_g$ transitions in this complex.

The most characteristic feature of the iron(II), cobalt(II) and nickel(II) complexes prepared, is their high-spin character. Analogous complexes of these metal ions with other ligands containing the –N=C–C=N– grouping display both high- and low-spin behaviour at room temperature [6, 7, 25–27], the spin state of the central metal ion being often dependent on minor structural variation in the chelating agent or on the nature of any other ligands present in the complex. The magnitude of the crystal field splitting produced by BZDH in $[Co(BZDH)_3]^{2+}$ has been reported to be 11000 cm^{-1} [7]. By considering this value and the pairing energies for cobalt(II) complexes involving ligands of the dimethine type (estimated to lie between 15000 and 16000

TABLE III. Solid State Magnetic Moments and Electronic Spectral Data of Complexes of Benzildihydrazone.

Complex	μ_{eff} (BM)[a]	Electronic Spectra (10^3 cm^{-1})						10 Dq (cm^{-1})	B(cm^{-1})	β
Iron(II) complexes		$^5T_{2g} \rightarrow {}^5E_g$					Other Bands			
$FeCl_2(BzDH)$	5.37	10.0 sh					20.2			
$FeBr_2(BZDH)_2$	5.28	9.5, 7.4					24.7, 21.8, 21.0, 16.4			
Cobalt(II) complexes		$^4T_{1g} \rightarrow {}^4T_{1g}(P), {}^4A_{2g}$		$^4T_{1g} \rightarrow {}^4T_{2g}$						
$CoCl_2(BZDH)_2$	5.00	18.6sh, 18.1		8.3			24.0	9265	772	0.79
$CoCl_2(BZDH)$	5.09	18.2, 17.1		8.4, 7.0			19.8	8745	774	0.80
$CoBr_2(BZDH)_2$	5.03	20.0, 19.0, 17.9		8.3			24.1	9260	792	0.81
$CoI_2(BZDH)_2$	4.96	20.0, 19.0, 18.0, 17.4sh, 16.4sh		8.2			24.7, 14.3sh	9190	779	0.80
$Co(NCS)_2(BZDH)_2$	5.23	21.8, 21.1sh, 20.1sh, 18.5, 17.2		9.4				10610	769	0.79
$Co(NO_3)_2(BZDH)_2$	4.94	21.1, 20.0, 19.2sh		9.2			24.1, 22.1	10365	810	0.83
Nickel(II) complexes		$^3A_{2g} \rightarrow {}^3T_{1g}(P)$	$^3A_{2g} \rightarrow {}^1T_{1g}$[b]	$^3A_{2g} \rightarrow {}^3T_{1g}(F)$	$^3A_{2g} \rightarrow {}^1E_g$[b]	$^3A_{2g} \rightarrow {}^3T_{2g}$				
$NiBr_2(BZDH)_2$	3.24	23.5		15.3		8.5	27.8	8500	802	0.77
$NiI_2(BZDH)_2$	3.04	23.8	20.0sh	15.5	11.0, 10.3sh	8.1	27.8	8100	862	0.83
$Ni(NCS)_2(BZDH)_2$	3.04	24.1	20.1sh	17.2		10.7, 10.2		10480	859	0.82
$Ni(NO_3)_2(BZDH)_2$	3.21	23.3	20.2sh	16.5	12.2sh	10.1		10205	911	0.87

[a] Measured at room temperature.

[b] Spin-forbidden bands frequently observed in octahedral nickel(II) complexes.

cm^{-1} [25]), it appears that the maximum splitting for the prepared cobalt(II) complexes is insufficient to cause pairing of spins in a regular octahedral environment.

Conclusions

The iron(II), cobalt(II) and nickel(II) complexes, which we have isolated, all have octahedral stereochemistry with bidentate N-methine coordination of BZDH. In this they resemble complexes of diacetyldihydrazone [6, 28]. The two ligands are similar in that they have $-NH_2$ groups which do not create excessive steric hindrance. The presence of large phenyl groups as opposed to methyl groups appears to have little steric effect; this is not unexpected as the phenyl groups are well away from the crowded areas. The main change upon switching from methyl to phenyl substituents is upon reactivity. With methyl groups, complexes form immediately and the number of ligand molecules which bind to the metal ions often increases with the amount of ligand used (up to a maximum of three). With phenyl groups, the reactions require heat and 1:1 adducts are formed via the 2:1 adducts and not directly as in the case of diacetyldihydrazone; these are in accord with the expected lower basicity of the methine-nitrogen atoms when phenyl groups are adjacent as compared when methyl groups with their large inductive (electron releasing) effect are present.

Our data for the bis-ligand complexes do not distinguish between the three possible octahedral structures, the *cis* and *trans* monomeric and the polymeric with bridging BZDH ligands. However, the insolubility of the complexes in organic solvents suggests rather polymeric natures. The mono-ligand octahedral iron(II) and cobalt(II) complexes must possess bridging chlorides as well as bridging BZDH ligands. The data available on $CdI_2(BZDH)$ cannot be assigned with certainty to any stereochemistry.

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