Inorganica Chimica Acta, 57 (1982) 21–24
©Elsevier Sequoia S.A., Lausanne – Printed in Switzerland

Co-ordination Compounds of Diacetyl Bis(dimethylhydrazone)

CHRISTINE N. ELGY, MARK R. HARRISON and DAVID NICHOLLS*

Donnan Laboratories, The University, Liverpool L69 3BX, U.K.

Received May 6, 1981

Complexes of diacetyl bis(dimethylhydrazone) (DDMH) have been prepared with iron(II), cobalt(II), nickel(II), copper(II) and zinc(II) salts. The complexes all have a metal to ligand ratio of 1:1 and are all believed to have tetrahedral structures with chelating DDMH.

Introduction

Complexes of the dihydrazone of diacetyl were first prepared by Stoufer and Busch [1] but have been studied more recently by Rai and Sahoo [2] who concluded that the complexes $M(DDH)_2X_2$ ($M = Ni, Co$; $X = Br, I, SCN, NO_3, BF_4$; DDH = diacetylhydrazone) have nearly octahedral arrangements of ligand atoms about the metal ions. The dimethylhydrazone of diacetyl (DDMH) has however been studied as a ligand only in recent years. Thus Dieck and Renk [3] have characterised the copper(I) chloride complex CuCl(DDMH) and there have been several studies of metal carbonyl-DDMH complexes [4–6] including a crystal structure determination on $Ni(CO)_2(DDMH)$ [7]. This latter work shows the ligand to act as bidentate through the methylene nitrogen atoms giving a tetrahedral environment around the nickel atom. We recently described co-ordination compounds of glyoxalbis(dimethylhydrazone) [8] in which we believe the ligand to be chelating via the nitrogen atoms of the C=N bonds. We report here complexes of diacetylbis(dimethylhydrazone) with iron(II), cobalt(II), nickel(II), copper(II) and zinc(II) salts.

---

*Author to whom correspondence should be addressed.

TABLE I. Analytical and Conductivity Data for Complexes of Diacetyl Bis(dimethylhydrazone).

Compound	Colour	Elemental analyses (%)[a]			Molar conductivities[b] Λ_M (ohm^{-1} mol^{-1} cm^2)
		C	H	N	
$FeCl_2(DDMH) \cdot H_2O$	red	30.3(30.5)	5.76(6.40)	17.6(17.8)	c
$FeBr_2(DDMH) \cdot H_2O$	orange–red	23.6(23.8)	4.47(4.99)	13.5(13.9)	c
$CoCl_2(DDMH)$	green	31.6(32.0)	5.79(6.05)	18.0(18.6)	4.3
$CoBr_2(DDMH)$	green	24.7(24.7)	4.50(4.66)	14.2(14.4)	4.9
$Co(NCS)_2(DDMH)$	green	34.7(34.8)	5.40(5.16)	23.7(23.9)	10.7
$NiCl_2(DDMH)$	brown	32.0(32.0)	6.07(6.04)	18.4(18.7)	0.2
$NiBr_2(DDMH)$	brown	24.1(24.7)	4.59(4.67)	13.7(14.4)	4.3
$Ni(NO_3)_2(DDMH)$	brown	26.2(27.2)	5.20(5.14)	23.6(23.8)	14.4
$Ni(NCS)_2(DDMH)$	brown	34.7(34.8)	5.48(5.22)	27.0(24.4)	15.3
$CuCl_2(DDMH)$	red–pink	31.1(31.5)	5.80(5.95)	18.1(18.4)	c
$CuBr_2(DDMH)$	black	23.1(24.4)	4.60(4.57)	13.9(14.2)	c
$ZnCl_2(DDMH)$	pale–yellow	31.5(31.4)	5.70(5.92)	17.9(18.3)	7.6
$ZnBr_2(DDMH)$	pale–yellow	24.8(24.3)	4.52(4.59)	14.0(14.2)	4.3
$Zn(NCS)_2(DDMH)$	yellow	34.3(34.1)	5.20(5.16)	23.2(23.9)	9.3

[a] Theoretical values in parentheses. [b] In nitromethane (approx. 10^{-3} *M* solutions). [c] Solutions unstable.

TABLE II. Spectral and Magnetic Data of Complexes of Diacetyl Bis(dimethylhydrazone).

Compound	Magnetic moment μ_{eff} (20 °C)	Electronic spectra (cm^{-1} × 10^3)								
		Solid state (reflectance)							Solution (CHCl$_3$); ε (l cm^{-1} mol^{-1}) in parentheses	
$FeCl_2(DDMH)\cdot H_2O$	5.36	43.8	35.4	26.5		6.8			6.8(670)	
$FeBr_2(DDMH)\cdot H_2O$	5.29	44.4	35.2	26.0		6.4			6.4(322)	
$CoCl_2(DDMH)$	4.80		34.0	27.5	15.0	9.7	7.2	5.9	14.4(350)	7.1(40)
$CoBr_2(DDMH)$	4.83		34.3	27.1	15.0	9.4	6.9		14.3(370)	7.1(40)
$Co(NCS)_2(DDMH)$	4.50		36.8	27.2	14.8	10.0	8.2	6.5	14.3(215)	8.0(70)
$NiCl_2(DDMH)$	3.37	33.5	28.5	20.4	16.0(sh)	9.6			9.5(40)	
$NiBr_2(DDMH)$	3.44		29.8	25.2		9.7			10.0(70)	
$Ni(NO_3)_2(DDMH)$	3.23	45.6	26.0			16.5(sh)		9.6	9.6(51)	
$Ni(NCS)_2(DDMH)$	3.43	43.3	20.6	19.5(sh)	11.2	9.9		6.9	6.9(60)	
$CuCl_2(DDMH)$	1.63	45.6	37.8	31.5	17.5	7.0				
$CuBr_2(DDMH)$	1.83	44.5		26.5		7.1				
$ZnCl_2(DDMH)$	diamagnetic	45.5	39.4	28.5	25.5					
$ZnBr_2(DDMH)$	diamagnetic	46.0	37.0	30.0						
$Zn(NCS)_2(DDMH)$	diamagnetic	43.5	33.5	26.7	24.5					

Results and Discussion

The complexes listed in Table I were most readily prepared by direct reaction between the metal salt and an excess of DDMH in hot ethanol. An alternative synthesis using the metal salt, diacetyl and dimethylhydrazine in ethanol under reflux (*i.e.* preparing the ligand *in situ*) proved to be more tedious and often yielded products contaminated with metal hydroxides or dimethylhydrazine complexes of the metals. The infrared spectra of the complexes confirm that all these 1:1 complexes are anhydrous with the exception of the iron(II) compounds which are monohydrated. The complexes are insoluble in benzene but dissolve in chloroform and nitromethane; the molar conductivities of the complexes in the latter solvent (Table I) are in accord with them being formulated as non-electrolytes.

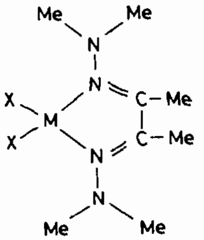
The magnetic moments (Table II) indicate that all the complexes are high spin, the iron(II) compounds are tetrahedral in the solid state as indicated by the single $^5E \rightarrow {}^5T_2$ transition at 6,800 cm^{-1} and the high values of the molar absorption coefficients for this peak in solution. Since the hydrazone is bidentate (see later) and the far IR spectra show the halogen atoms to be bonded to iron, the water molecules in these complexes cannot be co-ordinated to the iron atoms. The cobalt(II) complexes similarly show spectra which are typical of tetrahedral cobalt(II) compounds, the band at 15,000 cm^{-1} being assigned to the $^4A_2 \rightarrow {}^4T_1$ (P) transition with the band assignable to the $^4A_2 \rightarrow {}^4T_1$ (F) transition being split (by virtue of reduction of symmetry from T_d to C_{2v}) into bands representing the transitions to the $^4B_1$, $^4A_2$ and $^4B_2$ states [9]. The copper(II) complexes also exhibit spectra in the solid state characteristic of tetrahedral stereochemistry (the 7,000 cm^{-1} peak being assigned to the $^2T_2 \rightarrow {}^2E$ transition); unfortunately they decompose in solution so that measurements of solution spectra and absorption coefficients were not possible. The magnetic and spectral data on the nickel(II) complexes indicate tetrahedral stereochemistry with the $^3T_1 \rightarrow {}^3A_2$ transition being split most markedly in the thiocyanate complex; all the bands at ~9,600 cm^{-1} are broad. The $^3T_1 \rightarrow {}^3T_1$ (P) band (16,000–19,600 cm^{-1}) occurs as a shoulder on the more intense charge transfer band which occurs at around 26,000 cm^{-1} in all the complexes.

The IR spectra of the complexes are all very similar; they differ in the bands due to the anions and in the ν(M–X) region; the principal bands of interest are listed in Table III. The significant changes in the ligand bands upon complexing are the increases in ν(C=N) and ν(N–N). The assignment of the 1590 cm^{-1} band in DDMH to ν(C=N) is in agreement with other workers [5] and the movement of this band

TABLE III. Important Infrared Bands (cm^{-1}) in Complexes of Diacetyl Bis(dimethylhydrazone).

Compound	$\nu(CN)_{NCS}$	$\nu(C{=}N_2)$	$\nu(NN)$	$\nu(CS)$	$\delta(NCS)$	$\nu(MX)$	$\nu(MN)_{NCS}$
$FeCl_2(DDMH)\cdot H_2O$		1619	1154			360, 318	
$FeBr_2(DDMH)\cdot H_2O$		1612	1158			269	
$CoCl_2(DDMH)$		1620	1156			347, 319	
$CoBr_2(DDMH)$		1616	1159			260	
$Co(NCS)_2(DDMH)$	2023	1621	1150	862	486		339
$NiCl_2(DDMH)$		1621	1152			338, 310	
$NiBr_2(DDMH)$		1620	1152			262	
$Ni(NO_3)_2(DDMH)$		1626	1169			311, 286	
$Ni(NCS)_2(DDMH)$	2118, 2062	1623		879, 831	489, 479		338
$CuCl_2(DDMH)$		1628	1159			296	
$CuBr_2(DDMH)$		1609	1155			224	
$ZnCl_2(DDMH)$		1621	1149			336, 312	
$ZnBr_2(DDMH)$		1622	1158			241	
$Zn(NCS)_2(DDMH)$	2030	1629	1151	870	495, 482		319
DDMH (liquid)		1590	1120				

to higher wavenumbers is as has been observed in alkyl cyanide complexes [10] and in complexes of glyoxalbis(dimethylhydrazone) [8]. Similarly the strong band at 1120 cm^{-1} in the ligand we assign to ν(N–N) in accord with the assignments of ν(N–N) in formaldehyde dimethylhydrazone (1137 cm^{-1}) [11] and hydrazine (1098 cm^{-1}) [12]. The complexes all show a strong band around 1150 cm^{-1}; this shift to higher wavenumbers is very similar to that observed for ν(N–N) in hydrazine complexes [12]. Both of these shifts are compatible with the nitrogen of the C=N bond being the donor atom to the metal ions. The NMR spectra of the diamagnetic zinc conplexes in $CDCl_3$ all show two resonances due to methyl protons with an intensity ratio of 2:1 and lying downfield from the resonances in free DDMH (2.06 and 2.52 ppm downfield from TMS). It is evident therefore that the ligand is bonded symmetrically to the metal ions and must accordingly be bidentate. The tetrahedral 1:1 complexes thus almost certainly have the structure:



The metal–halogen stretching frequencies (Table III) are all in the range expected [13] for tetrahedral and non-bridging metal–halogens, thus supporting the above structure. The IR spectra of the thiocyanate complexes show ν(CN), ν(CS) and δ(NCS) vibrations all in the regions characteristic of N-bonded thiocyanate [13]. Further they show strong M–N stretching frequencies (not shown by the other complexes) above 300 cm^{-1} confirming their formulation as isothiocyanato complexes. The IR spectrum of $Ni(NO_3)_2(DDMH)$ shows strong metal–oxygen stretching vibrations in the far IR (Table III) confirming that the nitrate ions are bonded to the metal. Clearly two possible modes of bonding of the nitrate ions arise; bidentate nitrate ions would give a six co-ordinate structure around nickel while monodentate nitrate ions would give a four co-ordinate nickel(II) ion. The absorptions due to nitrate ions occur at 1512 cm^{-1} (NO_2 asym. stretch), 1268 cm^{-1} (NO_2 sym. stretch), 1037 cm^{-1} (N–O stretch), 808 cm^{-1} (out of plane rocking) and 759 cm^{-1} (NO_2 sym. bend); these are as found in complexes containing monodentate nitrate groups and the assignments are made [13] on that assumption. Complexes containing bidentate nitrate groups have ν_1 (N–O stretch) in the region 1550–1640 cm^{-1}; the absence of a band in this region in $Ni(NO_3)_2(DDMH)$ thus lends support for its formulation as a tetrahedral species having monodentate nitrate groups.

Experimental

Experimental techniques were as described previously [8]. Diacetyl bis(dimethylhydrazone) was prepared as previously described [4] and was purified by vacuum distillation, firstly from activated charcoal and then from barium oxide: IR spectrum: 2982(s), 2959(s), 2930(s), 2902(s), 2859(s), 2822(s), 2778(s), 1681(m), 1590(s), 1469(s), 1451(s), 1436(s), 1358(s), 1231(m), 1213(m), 1148(m), 1120(s), 1080(w), 1032(s), 992(s), 938(s), 854(m), 828(s), 670(m), 518(w), 532(w), 519(w), 491(w), 411(m), 316(w).

Two methods of preparation of complexes of DDMH were used. In the first method the metal salt was heated under reflux in ethanol with an excess of diacetyl and dimethylhydrazine (*i.e.* template synthesis). In these preparations the diacetyl had to be kept in >2:1 mole ratio with the dimethylhydrazine or else the product was contaminated with a dimethylhydrazine complex of the metal. If anhydrous salts were used crystalline complexes were obtained as precipitates upon cooling the ethanolic solutions; they were filtered off, washed with ethanol and dried in a vacuum desiccator over silica gel. The method did not work well if hydrated metal salts were used as starting materials; the products were often contaminated with metal hydroxides. In the second method of preparation, a solution of the metal salt in warm ethanol was treated with a 3–4 fold excess of DDMH; crystals were deposited immediately or upon cooling the solution to room temperature. The crystalline complexes obtained in this way were filtered off, washed and dried as in the template synthesis. As however this direct method of synthesis worked with both hydrated and anhydrous metal salts it was the preferred preparative method. The nickel(II) nitrate complex did not precipitate from ethanol; the deep red-brown solution of nickel nitrate and DDMH in ethanol was treated with diethyl ether until a deep red-brown oil formed. Three extractions of this oil with ether and trituration yielded the brown solid complex. The nickel(II) thiocyanate complex was prepared from hot aqueous solution because of the insolubility of the starting material in ethanol.

References

1 R. C. Stoufer and D. H. Busch, *J. Am. Chem. Soc., 78,* 646 (1956).

2 H. C. Rai and B. Sahoo, *J. Indian Chem. Soc., 53,* 646 (1976).

3 H. tom Dieck and I. W. Renk, *Chem. Ber., 104,* 92 (1971).

4 H. Bock and H. tom Dieck, *Chem. Ber., 100,* 228 (1967).

5 H. tom Dieck and I. W. Renk, *Chem. Ber., 104,* 110 (1971).

6 I. W. Renk and H. tom Dieck, *Chem. Ber., 105,* 1403 (1972).

7 H. D. Hausen and K. Krogmann, *Z. anorg. Chem., 389,* 247 (1972).

8 Christine N. Elgy and David Nicholls, *J. Inorg. Chem. Nuclear Chem., 43,* 2025 (1981).

9 A. B. P. Lever, Inorganic Electronic Spectroscopy, Elsevier, Amsterdam, 1968.

10 R. A. Walton, *Quarterly Reviews, 19,* 126 (1965).

11 W. C. Harris, F. L. Glenn and L. B. Knight, *Spectrochim. Acta, 31A,* 11 (1975).

12 D. N. Sathyanarayana and D. Nicholls, *Spectrochim. Acta, 34A,* 263 (1978).

13 J. R. Ferraro, Low Frequency Vibrations of Inorganic and Coordination Compounds, Plenum Press, New York, 1971.