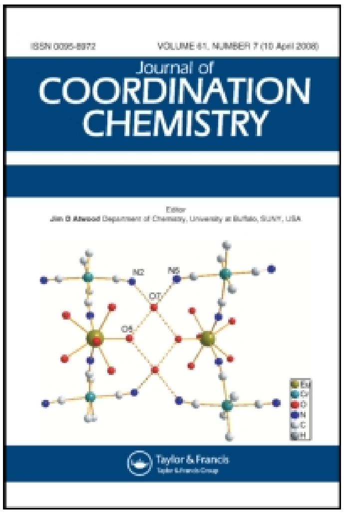

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BIACETYLDIHYDRAZONE AND BRIDGE CYANIDE COMPLEXES

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Dinuclear complexes of biacetyldihydrazone (BdH) and bridging cyanide groups, $(BdH)_2M(NC)_2Ni(CN)_2.H_2O$, M=Co(II), Ni(II) or Zn(II); $(BdH)M(NC)_2Ni(CN)_2.H_2O$, M=Cu(II) or Zn(II); $(BdH)Cu(NC)_2Zn(CN)_2.H_2O$ and $(BdH)_2Ni(CN)_2Zn(CN)_2.H_2O$ were prepared by reaction of $[M(BdH)_3](NO_3)_2$ and $K_2[Ni(CN)_4]$ or $K_2[Zn(CN)_2]$. The complexes are insoluble and have been characterized by infrared and electronic spectroscopies. Magnetic subsceptibilities in the 4.2–290K range show Curie - Weiss behaviour for the paramagnetic samples.

Keywords: cyanide; biacetyldihydrazone; dimers

INTRODUCTION

Biacetyldihydrazone ($H_2NNC{=}Me{-}CMe{=}NNH_2$) is a bidentate ligand with two imine *N*-atom donors coordinated to a metal atom. For the first transition element series, complexes have been reported[1–3] and are of high or low spin according to the nature of metal.

In previous communications[4–6] we described the synthesis and characterization of $[M(BdH)_3](NO_3)_2$, M=cobalt(II), nickel(II), copper(II) or zinc(II), BdH=biacetyldihydrazone; $[Fe(BdH)_3](NO_3)_3$; $[M(BdH)_3][Ni(dto)_2]$, M=cobalt(II), nickel(II) or zinc(II), dto=dithiooxalate; $(BdH)_2Cu(dto)Ni(dto)$ and $[Fe(BdH)_3]_2[Ni(dto)_2]_3$. The latter were prepared by reactions of nitrates with $K_2[Ni(dto)_2]$. All complexes are ionic. The $[M(BdH)_3]^{n+}$ cation remains unchanged. Only the copper(II) complex is dinuclear with a bridge dto^{2-} and two BdH molecules.

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In this paper we describe the interaction of nitrates with $K_2[Ni(CN)_2]$ and $K_2[Zn(CN)_4]$. In this case the $[M(BdH)_3]^{2+}$ cations are affected. A BdH molecule is released and dinuclear complexes, with two bridging cyanide groups, are formed in the case of $(BdH)_2M(NC)_2Ni(CN)_2.H_2O$, M=cobalt(II), nickel (II) or zinc(II) and $(BdH)_2Ni(NC)_2Zn(CN)_2.H_2O$. For copper(II) complexes two BdH molecules are released and $(BdH)Cu(NC)_2M(CN)_2.H_2O$, M=nickel(II) or zinc(II) is formed. $(BdH)Zn(NC)_2Ni(CN)_2.H_2O$ is obtained as well.

EXPERIMENTAL

Preparation of Complexes

Biacetyldihydrazone was prepared according to the Busch and Bailar method.[7] $K_2[Ni(CN)_4]$ and $K_2[Zn(CN)_4]$ were obtained from the reaction of nickel chloride and zinc nitrate respectively, with potassium cyanide in water.[8–9] $[M(BdH)_3](NO_3)_2$, M=cobalt(II), nickel(II), copper(II) and zinc(II) were obtained according to described methods.[4, 10]

$(BdH)_2Co(NC)_2Ni(CN)_2.H_2O$

To an aqueous solution of 6 mmol of $K_2[Ni(CN)_4].H_2O$ was added 3 mmol of $[Co(BdH)_3](NO_3)_2.H_2O$ in water. The precipitate formed was filtered and the solution was stirred 24h. The new precipitate formed was filtered, washed with water and dried *in vacuo* over $CaCl_2$. Colour: rose. Yield: 56%. Dec.: 215°C. Anal. calc. (%): C, 30.80; H, 4.74; N, 35.91. Found: C, 30.94; H, 4.51; N, 35.75.

$(BdH)_2M(NC)_2Ni(CN)_2$. M=nickel(II) or zinc(II)

An aqueous solution of 3 mmol of $K_2[Ni(CN)_4].H_2O$ was added to 3 mmol of $[M(BdH)_3](NO_3)_2$ in water. After 15 minutes stirring, the precipitate was filtered, washed with water and dried *in vacuo* over $CaCl_2$. For M=Ni,colour: rose. Yield: 73%. Dec.: 215°C. Anal. calc. (%): C, 32.04; H, 4.48; N, 37.37. Found: C, 31.42; H, 4.47; N, 36.60. For M=Zn, colour: yellow. Yield: 56%. Dec.: 222°C. Anal. calc. (%): C, 30.38; H, 4.67; N, 35.42. Found: C, 30.84; H, 4.89; N, 35.38.

$(BdH)Zn(NC)_2Ni(CN)_2.H_2O$

Some 3 mmol $[Zn(BdH)_3](NO_3)_2$ in water were added to an aqueous solution of $K_2[Ni(CN)_4].H_2O$ in 1:1 proportion. The precipitate was filtered, washed with water and dried *in vacuo* over $CaCl_2$. Colour: white. Yield: 68%. Dec.: 208°C. Anal. calc. (%): C, 26.67; H, 3.36; N, 31.10. Found: C, 26.66; H, 3.27; N, 30.99.

(BdH)Cu(NC)$_2$M(CN)$_2$.H$_2$O.M= nickel(II) or zinc(II)

An aqueous solution of 3 mmol $K_2[M(CN)_4]$ was added to an ice cold aqueous solution of 3 mmol $[Cu(BdH)_3](NO_3)_2.H_2O$. The mixture was stirred in an ice bath for 1 h. The precipitate was filtered, washed with water and dried *in vacuo* over $CaCl_2$. For M=Ni, colour: green. Yield: 85%. Dec.: 212°C. Anal. calc. (%): C, 26.80; H, 3.37; N, 31.26. Found: C, 26.78; H, 3.28; N, 30.04. For M=Zn, colour: green. Yield: 85%. Dec.: 163°C. Anal. calc. (%): C, 26.31; H, 3.31; N, 30.68. Found: C, 26.86; H, 3.21; N, 30.64.

(BdH)$_2$Ni(NC)$_2$Zn(CN)$_2$.H$_2$O

To an aqueous solution of 3 mmol $K_2[Zn(CN)_4]$, an aqueous solution of 3 mmol $[Ni(BdH)_3](NO_3)_2$ was added. After 1 minute, the bright rose precipitate was filtered, washed with water and dried *in vacuo* over $CaCl_2$. Colour: rose. Yield: 52%. Dec.: 177°C. Anal. calc. (%): C, 30.38; H, 4.67; N, 35.42. Found: C, 30.48; H, 4.51; N, 35.23. By the same reaction, but after 1 h of stirring, a yellow precipitate was obtained. When addition of $K_2[Zn(CN)_4]$ and $[Ni(BdH)_3](NO_3)_2$ aqueous solutions was made in the opposite order, the same yellow precipitate was formed. It was filtered, washed with water and dried *in vacuo* over $CaCl_2$. The yellow compound was shown to be the previously described complex, $(BdH)_2Zn(NC)_2Ni(CN)_2$, instead of the expected species $(BdH)_2Ni(NC)_2Zn(CN)_2$. Its diamagnetic character and thermal analysis, X-ray powder diffraction pattern and spectroscopic data confirm this assignation.

Physical Measurements

C, H and N were analysed using a Perkin Elmer 240C Elemental Analyzer. Melting points were measured on a Buchi 510 instrument. Infrared spectra were recorded, in the 4000 – 200 cm^{-1} region, on a Perkin Elmer 598 spectrophotometer with KBr pellets. Electronic spectra, as diffuse reflectance, were registered on a Schimadzu UV – 265 FW instrument.

Magnetic subsceptibilities were determined with a DSM8 susceptometer, with a Drusch M 1119 power source and an Oxford ITC4 temperature controller. Diamagnetic corrections were applied.[11] Epr spectra were recorded for the cobalt(II) complex with a spectrometer Bruker ESP 300.

RESULTS AND DISCUSSION

Reactions between $[M(BdH)_3](NO_3)_2$ and $K_2[M'(CN)_4]$ cause one or two BdH molecules to be released and the dinuclear complexes $(BdH)_2M(NC)_2M'(CN)_2$, (M=Co, Ni or Zn and M'=Ni; M=Ni and M'=Zn) and $(BdH)M(NC)_2M'(CN)_2$, (M=Cu or Zn and M'=Ni; M=Cu and M'=Zn) are formed. In the Ni, Zn complex, yellow $(BdH)_2Zn(NC)_2Ni(CN)_2$ was obtained, regardless of the fact that the initial reactants were $[Ni(BdH)_3](NO_3)_2$ and $K_2[Zn(CN)_4]$ or $[Zn(BdH)_3](NO_3)_2$ and $K_2[Ni(CN)_4]$. The rose compound $(BdH)_2$ $Ni(NC)_2Zn(CN)_2$ was obtained after a short reaction time between $[Ni(BdH)_3](NO_3)_2$ and $K_2[Zn(CN)_4]$. In the solid state the rose compund is stable, but in suspension undergoes the following reaction.

$$(BdH)_2Ni(NC)_2Zn(CN)_2 \longrightarrow (BdH)_2Zn(NC)_2Ni(CN)_2$$

All yellow samples are diamagnetic, X-ray diffaractograms, ir spectra and thermal analysis curves are the same. Because all complexes are insoluble in the usual solvents, it was not possible to carry out solution conductivity measurements, electronic spectra in solution or cyclic voltametry.

Infrared Spectra

Infrared data are summarized in Table I. Biacetyldidydrazone absorptions do not show any significant variation with regard to nitrate complexes.[4–5] The most characteristic and for cyanide complexes is $\nu(C{\equiv}N)$.[12–13] All complexes show two bands, assigned to $\nu(C{\equiv}N)$, in the 2120 - 2190 cm^{-1} range. The higher frequency one is assigned to the bridging group. For complexes with only one coordinated BdH molecule, $(BdH)Cu(NC)_2Ni(CN)_2.H_2O$, $(BdH) Cu(NC)_2Zn(CN)_2.H_2O$ and $(BdH) Zn(NC)_2Ni(CN)_2.H_2O$, the $\nu(C{\equiv}N)$ bridging band shifts to higher values.

Electronic Spectra

Only diffuse reflectance spectra were recorded, because of the low solubility of the complexes. Results are summarized in Table II. The $K_2[Zn(CN)_4]$ spectrum shows two charge transfer bands (M → L) in the ultraviolet region, according to a d^{10} configuration with tetrahedral cordination.[14] The complex spectra show a very broad band in the ultraviolet region, which includes $M \rightarrow CN^-$ charge transfer bands and the $\pi \rightarrow \pi^*$ band of biacetyldihydrazone. The d — d bands in the complexes are observed at lower energies than those of the nitrates.[5] The cyanide ligand coordinated through the nitrogen atom behaves as a medium field ligand, somewhat weaker than biacetyldihydrazone and the Δ value decreases with substitution of a BdH ligand by two *N*-coordinated CN-groups. The spectrum of the dinickel complex shows d — d bands assigned to pseudo-octathedral $^3A_{2g} \rightarrow {}^3T_{2g}(F)$ and $^3A_{2g} \rightarrow {}^3T_{2g}(F)$ transitions.

Although the formula $(BdH)Cu(NC)_2Ni(CN)_2 \cdot H_2O$ suggest four coordination for copper(II), electronic spectra and the green colour correspond to a pseudooctahedral coordination. In the solid state may have interactions which define hexacoordination. For $(BdH)Cu(NC)_2Zn(CN)_2.H_2O$ similar results were obtained. For $(BdH)_2Ni(NC)_2Zn(CN)_2.H_2O$, two d — d bands, assigned to $^3A_{2g} \rightarrow {}^3T_{2g}(F)$ and $^3A_{2g} \rightarrow {}^3T_{2g}(F)$ transitions in an octahedral fields, are observed. *N*-coordinated CN^- behaves as a medium field ligand.

Magnetic Measurements

Magnetic susceptibilities of powdered samples were measured over the temperature range 4.2–290K. C and θ were calculated from the Curie-Weiss law, $\chi = C/(T - \theta)$, by plotting χ_M^{-1} *versus* T. Results are summarized in Table II. Magnetic moments were calculated from C values. $(BdH)_2Zn(NC)_2Ni(CN)_2.H_2O$ and (BdH) $Zn(NC)_2Ni(CN)_2.H_2O$ are diamagnetic. These results confirm the conservation of square-planar and diamagnetic character of the $(NC)_2Ni(CN)_2$ group. All other complexes obey the Curie-Weiss law. The cobalt(II) complex, moment does not vary with temperature and corresponds to a high spin state,[4] T_1. E.s.r. spectra show no signal. Results for $[Co(BdH)_3](NO_3)_2.H_2O$ and $[Co(BdH)_2][Ni(dto)_2].H_2O$ were different.[6] They showed anomalous magnetic susceptibility *versus* temperature; this was interpreted on the basis of a spin crossover system with an equilibrium between high spin (quartet, $S = 3/2$) and low spin (doublet, $S = 1/2$) states.

For $(BdH)_2Co(NC)_2Ni(CN)_2.H_2O$, substitution of a BdH ligand in $[Co(BdH)_3]^{2+}$ by two CN^- groups coordinated through the nitrogen atom causes a crystal field decrease and a shift from the spin crossover situation to a high spin state as the only species in the system. $(BdH)_2Ni(NC)_2Zn(CN)_2$ is paramagnetic, with a magnetic moment assignable to a d^8 configuration in a near octahedral field, determinated by two BdH molecules and two nitrogen atoms of bridging cyanides.

Acknowledgments

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TABLE I Characteristic IR bands for the complexes (cm^{-1})

Assignment	$L_2Co(NC)_2$ $Ni(CN)_2 \cdot H_2O$	$L_2Ni(NC)_2$ $Ni(CN)_2$	$L\ Cu(NC)_2$ $Ni(CN)_2 \cdot H_2O$	$L\ Zn(NC)_2$ $Ni(CN)_2 \cdot H_2O$	$L_2Zn(NC)_2$ $Ni(CN)_2 \cdot H_2O$	$L_2Ni(NC)_2$ $Zn(CN)_2 \cdot H_2O$	$LCu(NC)_2$ $Zn(CN)_2 \cdot H_2O$
H_20	3600br		3525br	3567br	3556br	3500br	3610br
$\nu_a NH_2$					3434sh		
	3415s	3415s	3427s	3408s	3408s	3409s	3399s
	3378sh	3377sh	3407sh		3378sh	3370s	
$\nu_s NH_2$	3310s	3310s	3300s	3312s	3312s	3308s	3312s
	3283s	3280s			3285sh		
	3208s	3206s	3205s	3189s	3215s	3207s	3223s
ν CH	2923w	2925w	2926w	2928w	2929w	2925w	2928w
ν C≡N	2155s	2154s	2181s	2172s	2153s	2189s	2189sh
	2124s	2124s	2126s	2137s	2124s	2160m	2123s
$\delta_a NH_2$				1642sh		1641s	
νC=N (BdH)	1612s	1613s	1616s	1616s	1616s	1605s	1615s
δ_a C—CH_3	1439m	1438m	1437m	1437m	1437m	1445m	1437m
δ_s C—CH_3	1371m	1371m	1379m	1376s	1370s	1373s	1375m
	1286w	1286w	1305w	1296w	1286w	1277m	1298w
	1259m	1260m	1258m	1262w	1257m	1250w	1265w
	1225w	1223w	1241w	1217w	1217w	1224m	1219w
	1101s	1101s	1108m	1104s	1099s	1102s	1102m
	1005w	1005w	1005w	1010w	1005w	1005m	1007w
	960w	958w	962w	960w	958w	963m	963m
ν N—N	1149s	1149s	1167m	1157s	1147s	1153s	1149m
$\rho_r NH_2$	778m	779m	791m	776m	778m	775m	777m
	742br	732br	720br	720br	720br	712br	721br
	682m	682m	687w	668w	668w	664w	668w
	587w	586w	584w		582w	583w	587w
	488m	468m	475s		481m	472s	468s
ν NiC	546 w	548w	536w	531s	539w	543m	
δ NiCN	453sh	454sh		455m	450sh		
	423s	424s	427s	428s	420s	409s	
	308w	309w	318m				
				280w	278w		

TABLE I *(Continued)*

Assignment	*$L_2Co(NC)_2$ $Ni(CN)_2{\cdot}H_2O$*	*$L_2Ni(NC)_2$ $Ni(CN)_2$*	*$L\,Cu(NC)_2$ $Ni(CN)_2{\cdot}H_2O$*	*$L\,Zn(NC)_2$ $Ni(CN)_2{\cdot}H_2O$*	*$L_2Zn(NC)_2$ $Ni(CN)_2{\cdot}H_2O$*	*$L_2Ni(NC)_2$ $Zn(CN)_2{\cdot}H_2O$*	*$L\,Cu(NC)_2$ $Zn(CN)_2{\cdot}H_2O$*
	255w	255w					
ν ZnC						378 m	
δ ZnCN						315 w	

L = biacetyldihydrazone; s = strong; m = medium; w = weak; sh = shoulder; br = broad.

TABLE II Diffuse reflectance data and magnetic results

Compound	λ_{max} *(nm)*	*Assignment*	*C* *($K\ cm^3 mol^{-1}$)*	θ *(K)*	μ *(MB)*[a]
$(BdH)_2Co(NC)_2Ni(CN)_2H_2O$	240 – 330$^{(br)}$	C.T. + π → π*	1.221	–2.10	3.13
	525	C.T. (Co → Bdh)			
$(BdH)_2Ni(NC)_2Ni(CN)_2$	250 – 330$^{(br)}$	C.T. + π → π*	1.036	–2.70	2.88
	520	$^3A_{2g} \rightarrow {}^3T_{1g}(F)$			
	840	$^3A_{2g} \rightarrow {}^3T_{2g}(F)$			
$(BdH)Cu(NC)_2Ni(CN)_2H_2O$	200 – 350$^{(br)}$	C.T. + π → π*	0.443	–1.25	1.88
	475	C.T. (Cu → BdH)			
	640	$^2E_g \rightarrow {}^2T_{2g}$			
$(BdH)Zn(NC)_2Ni(CN)_2{\cdot}H_2O$	240 – 320$^{(br)}$	C.T. + π → π*	Diamagnetic		
$(BdH)_2Zn(NC)_2Ni(CN)_2{\cdot}H_2O$	240 – 330$^{(br)}$	C.T.+ π → π*	Diamagnetic		
$(BdH)_2Ni(NC)_2Zn(CN)_2{\cdot}H_2O$	200	C.T.(Ni → CN)	0.989	–0.38	2.81
	250 – 325$^{(br)}$	C.T. + π → π*			
	525	$^3A_{2g} \rightarrow {}^2T_{1g}(F)$			
	825	$^3A_{2g} \rightarrow {}^3T_{1g}(F)$			
$(BdH)Cu(NC)_2Zn(CN)_2H_2O$	300	π → π* + C.T.(Zn → CN)	0.331	9.45	1.63
	445$^{(sh)}$	C.T. (Cu → Bdh)			
	720	$^2E_g \rightarrow {}^2T_{2g}$			

Here, sh = shoulder, br = broad. [a]From calculated C values.

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