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New Complexes of Cobalt(II) and Nickel(II) Salts with N,N'-Diethylurea

J. P. BARBIER and R. HUGEL
Laboratoire de Chimie Minérale, Université de Reims, BP 347, 51062 REIMS, Cedex, France

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The following coordination compounds of Co(II) and Ni(II) with N,N'-diethylurea (DEU) have been prepared: $M(DEU)_3X_2$ (X = Cl, Br, I, SCN for M = Co(II) and X = Cl, Br, I for M = Ni(II)), $Ni(DEU)_6X_2$ with X = Br, I, ClO_4, $Co(DEU)_6(ClO_4)_2$ and $Ni(DEU)_4(NCS)_2$. Electronic spectra, IR spectra (4000–250 cm^{-1}), paramagnetic susceptibility and powder diffraction patterns were studied. The ligand is always bonded through the oxygen atom. Electronic and IR spectra have shown mixed octahedral–tetrahedral coordination for the metal in $M(DEU)_3X_2$ complexes that must be written as $[MDEU_6][MX_4]$ and octahedral coordination in the remaining compounds.

Introduction

In a previous work we have studied the complexes of manganese(II) with N,N'-diethylurea[1] and found two types of compounds which have been shown to be oxygen bonded and mixed octahedral–tetrahedral for $Mn(DEU)_3X_2$ and octahedral for $Mn(DEU)_6X_2$. The coordination compounds of DEU with other transition metal ions were unknown except for the octahedral–tetrahedral $[CoDEU_6][CoCl_4]$[2]. We have undertaken a study of Ni(II) and Co(II) complexes with DEU to show the effect of the metal ion on the coordination of this ligand and for comparison of the results with those already obtained[1] for manganese(II).

Experimental

N,N'-diethylurea was recrystallized from water. Ni(II) thiocyanate and Co(II) iodide were obtained respectively after reaction of $Ba(SCN)_2$ with $NiSO_4$ and BaI_2 with $CoSO_4$. All Ni(II) and Co(II) salts were dehydrated under vacuum for the iodides, or by heating for the other halides, or by addition of triethylorthoformate for the perchlorates[3].

The crystallization of the complexes was induced by addition of cold diethylether and the solids were washed with diethylether and dried under vacuum (0.2 mm) at room temperature except for the unstable $Ni(DEU)_6I_2$.

Hexakis(N,N'-diethylurea)nickel(II) (or Cobalt(II)) Tetrahalonickelate (or cobaltate)

DEU (0.025 mol, 2.9 g) was added to an ethanolic metal halide (0.005 mol) solution and refluxed for two hours.

TABLE I. Analytical Results for Ni(II) and Co(II) N,N'-Diethylurea Complexes.

Compound	Color	Melting Point °C	% Carbon		% Hydrogen		% Nitrogen		% Metal		% Halogen	
			Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
$NiDEU_3Cl_2$	Blue	181°	37.68	37.88	7.59	7.64	17.58	17.49	12.3	12.3	14.8	14.8
$NiDEU_3Br_2$	Pale blue	178°	31.77	31.64	6.40	6.50	14.82	14.85	10.3	10.3	28.2	28.1
$NiDEU_3I_2$	Red	181°	27.26	27.46	5.49	5.46	12.71	12.60	8.9	8.8	38.4	37.9
$NiDEU_4(NCS)_2$	Blue – Green	142°	41.32	41.01	7.57	7.58	21.90	21.80	9.2	9.3	–	–
$NiDEU_6Br_2$	Green	128°	39.36	39.12	7.93	8.03	18.36	18.29	6.4	6.6	17.5	17.6
$NiDEU_6I_2$	Green	151°	35.69	35.67	7.19	7.14	16.65	16.74	5.8	5,9	25.2	25.1
$NiDEU_6(ClO_4)_2$	Green	189°	37.75	37.89	7.60	7.69	17.61	17.74	6.2	6.2	–	–
$CoDEU_3Cl_2$	Blue	117°	37.67	37.64	7.59	7.50	17.57	17.52	12.3	12.4	14.8	15.0
$CoDEU_3Br_2$	Pale blue	103°	31.76	31.91	6.40	6.58	14.82	14.83	10.4	10.3	28.2	28.0
$CoDEU_3I_2$	Dark green	102°	27.25	27.41	5.49	5.56	12.71	12.77	8.9	8.7	38.4	37.8
$CoDEU_3(NCS)_2$	Dark blue	107°	39.00	39.14	6.93	7.00	21.40	21.48	11.3	11.3	–	–
$CoDEU_6(ClO_4)_2$	Pink	158°	37.74	37.78	7.60	7.56	17.60	17.69	6.2	6.2	–	–

Hexakis(N,N'-diethylurea)nickel(II) Bromide and Iodide

DEU (0.05 mol, 5.8 g) and the nickel halide (0.005 mol) were dissolved in 20 ml absolute ethanol and refluxed during half an hour.

Diisothiocyanato-tetrakis(N,N'-diethylurea)nickel(II)

$Ni(SCN)_2$ (0.005 mol) and DEU (0.035 mol) were stirred and refluxed in absolute ethanol during three hours.

Hexakis(N,N'-diethylurea)nickel(II) or Cobalt(II)) Perchlorate

These compounds were prepared like $Mn(DEU)_6(ClO_4)_2$[1].

Analytical

Nickel was determined by electrodeposition and cobalt by EDTA titration using murexide indicator or by atomic absorption for thiocyanate compounds. The halides were determined by potentiometry with silver nitrate (Table I).

Results and Discussion

Electronic Spectra

Electronic spectra were obtained on a Beckman DK 2A Spectrophotometer with a reflectance attachment (30 000–4000 cm^{-1}, Tables II and III).

The weak bands of $[CoDEU_6]^{2+}$ are masked by the strong absorption of the tetrahalo cobalt(II) ions. For the octahedral compound $Co(DEU)_6(ClO_4)_2$ the ν_1 band ($^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$) is located at about 8000 cm^{-1} and the ν_3 band ($^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$) at about 19 000 cm^{-1} with a shoulder at about 20 800 cm^{-1}.

The ligand-field parameters are listed on Table IV. Δ and B are obtained from transition energy ratios given by Lever[4] (using ν_3/ν_1 ratio for octahedral Ni(II) and Co(II) compounds and ν_3/ν_2 ratio for tetrahalonickelate ion).

The ν_2 band for $[CoX_4]^{2-}$ is very broad and the energy of this transition is not determined with precision. The determination of Δ_t is made from the energy diagram proposed by Cotton *et al.*[5] obtained from

TABLE II. Electronic Reflectance Spectra of Ni(II) Compounds (wavenumbers in cm^{-1}).

Compound	ν_3 Band (oct.) $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$	ν_2 Band (oct.) $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ + forbidden transition	ν_1 Band (oct.) $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$	ν_3 Band (tetr.) $^3T_1(F) \rightarrow {}^3T_1(P)$	ν_2 Band (tetr.) $^3T_1(F) \rightarrow {}^3A_2(F)$
$[NiDEU_6][NiCl_4]$	24000	b	(8400)sh	14950	7650
$[NiDEU_6][NiBr_4]$	a	b	(8400)sh	14000	7200
$[NiDEU_6][NiI_4]$	a	b	(8400)sh	12750	7400
$NiDEU_4(NCS)_2$	24700	14900 13600	9300		
$NiDEU_6Br_2$	24000	13400	8400		
$NiDEU_6I_2$	(24100)sh	12300	8400		
$NiDEU_6(ClO_4)_2$	24000	12900	8400		

[a] Masked by charge transfer band of $[NiX_4]^{2-}$. [b] Masked by ν_3 band of $[NiX_4]^{2-}$.

TABLE III. Electronic Reflectance Spectra of Co(II) Compounds (wavenumbers in cm^{-1}).

Compound	$^4A_2(F) \rightarrow$ Doublet States				ν_3 Band (tetr.) $^4A_2(F) \rightarrow {}^4T_1(P)$	ν_2 Band (tetr.) $^4A_2(F) \rightarrow {}^4T_1(F)$ very broad absorption with a maximum around
$[CoDEU_6][CoCl_4]$	26100	24300	22050	18900	15150	6400
$[CoDEU_6][CoBr_4]$	24900	23250 22800	21300 21050 20600	18350	14450	5900
$[CoDEU_6][CoI_4]$		21600	20950 { 19900 19100	18250	13300	5500
$[CoDEU_6][Co(NCS)_4]$			22950	21750sh 20100	16450	9500

TABLE IV. Ligand-field Parameters (accuracy 50 cm^{-1} for Δ, 10 cm^{-1} for B).

Compound	Δ_o	Δ_t	B	β^a
$[NiDEU_6]^{2+}$	8400	–	840	0.82
$NiDEU_4(NCS)_2$	9300	–	790	0.77
$[NiCl_4]^{2-}$	–	4180	810	0.79
$[NiBr_4]^{2-}$	–	3890	750	0.73
$[NiI_4]^{2-}$	–	3980	660	0.64
$[CoDEU_6]^{2+}$	9100	–	810	0.83
$[CoCl_4]^{2-}$	–	3650	700	0.72
$[CoBr_4]^{2-}$	–	3150	700	0.72
$[CoI_4]^{2-}$	–	2400	690	0.71
$[Co(NCS)_4]^{2-}$	–	4600	700	0.72

$^a B_0$ value for free Ni(II)ion: 1030 cm^{-1}; B_0 value for free Co(II)ion: 971 cm^{-1}.

Tanabe, Sugano's[6] secular equation and B is calculated from the value of Δ_t and the ν_3 transition energy.

The results agree very well those of Cotton *et al.* for tetrahalo ions[5,7]. The Δ_o value for $Ni(DEU)_4(NCS)_2$ is in good agreement with thiocyanate coordination through nitrogen and the B value with a distorted octahedral geometry.

Infrared Spectra

Infrared spectra (Table V) were recorded on a Perkin–Elmer 521 in KBr discs or Nujol mulls (4000–600 cm^{-1}) and in polyethylene discs (600–250 cm^{-1}).

Band shifts ($\nu_{C=O}$ decreases, δ_{N-H}, ν_{C-N} and δ_{N-C-N} increase) indicate a coordination through the oxygen atom[1]. All these spectra and those of Mn(II) compounds[1] are very similar except for the N–H stretching: the slight difference is probably due to hydrogen bonding between the octahedral cation and the anion.

The C–N stretching and N–C–S bending occur at 2100 cm^{-1} and 495, 478, 463 cm^{-1} in $Ni(DEU)_4(NCS)_2$, confirming the nitrogen coordination of the NCS^- anion[8]. The band at 2100 cm^{-1}, sharp and unsplit, is indicative of a *trans*-geometry. For the tetrahedral anion $[Co(NCS)_4]^{2-}$, the C–N stretching at 2070 cm^{-1}, the N–C–S bending at 480 cm^{-1} and the Co–N stretching at 308 cm^{-1} are in very good agreement with the value given in the literature[8,9].

The far-IR spectra of $Ni(DEU)_3X_2$ compounds were recorded (400–50 cm^{-1}). The Ni–X vibration frequencies (Ni–Cl: 288–122, Ni–Br: 222–105 and Ni–I: 192–96) compare favorably with those of the anion $[NiX_4]^{2-}$ described by Sabatini *et al.*[10].

Magnetic Susceptibility

The magnetic data at room temperature (20° C) are listed in Table VI. The observed susceptibilities were corrected for diamagnetism and temperature independent paramagnetism (t.i.p.) for tetrahedral cobalt(II) and octahedral nickel(II). The t.i.p. corrections were calculated in the usual manner from the Δ values in Table IV using the relation,[11] t.i.p. = $2.09/\Delta$.

The magnetic susceptibility of $[NiX_4]^{2-}$ species can be calculated after deduction of the susceptibility of the $[NiDEU_6]^{2+}$ cation in the mixed octahedral–tetrahedral compounds. The obtained values (admitting a Curie–Weiss constant near 0° K for Ni(II) compounds) are 3.80 B.M. for $[NiCl_4]^{2-}$ ion, 3.75 B.M. for $[NiBr_4]^{2-}$ ion and 3.45 B.M. for $[NiI_4]^{2-}$ ion. These results are in very good agreement with those of Goodgame *et al.*[7] and Gill and Nyholm[12].

The magnetic moments of the cobalt compounds are not determined because the Curie–Weiss constant is often higher than 10° K for this compounds. Nevertheless, the magnetic susceptibility can be ranged as $X_M[CoCl_4]^{2-} > X_M[CoBr_4]^{2-} \sim X_M[CoI_4]^{2-} > X_M[Co(NCS)_4]^{2-}$, this order being different from the one found usually in literature[5,12], $X_M[CoI_4]^{2-} > X_M[CoBr_4]^{2-} > X_M[CoCl_4]^{2-} > X_M[Co(NCS)_4]^{2-}$. Some inter-

TABLE V. Significant Bands in Infrared Spectra of Ni(II) and Co(II) Compounds.

Compound	ν_{N-H} Stretching	$\nu_{C=O}$ Stretching	S_{N-H} Bending	ν_{C-N} Amide III Band	S_{N-C-N} Skeleton
DEU ($CHCl_3$)	3445 vs, 3390 sh	1665 vs	1545 vs	1320–1300 m	1140 w
$NiDEU_3Cl_2$	3340 vs, 3130 vw	1625 vs	1570 vs	1350–1338 s, 1290 s	1160–1140 s
$NiDEU_3Br_2$	3380–3330 vs, 3130 vw	1625 vs	1570 vs	1350–1338 s, 1295 s	1160–1142 s
$NiDEU_6Br_2$	3330–3250 vs, 3135 vw	1625 vs	1575 vs	1352–1340 s, 1295 s	1160–1142 s
$NiDEU_3I_2$	3390–3340 vs	1625 vs	1568 vs	1350–1338 s, 1295 s	1160–1140 s
$NiDEU_6I_2$	3330–3270 vs	1625 vs	1570 vs	1350–1338 s, 1290 s	1158–1140 s
$NiDEU_4(NCS)_2$	3400–3370 vs	1630 vs	1555 vs	1355–1335 s, 1285 s	1160–1140 s
$NiDEU_6(ClO_4)_2$	3400 sh, 3330 vs, 3290 sh	1625 vs	1570 vs	1345–1330 s, 1290–1275 m	$\nu_3ClO_4^-$
$CoDEU_3Cl_2$	3345 vs, 3130 vw	1625 vs	1565 vs	1350–1335 s, 1290 s	1160–1140 s
$CoDEU_3Br_2$	3380–3330 vs, 3130 vw	1625 vs	1565 vs	1350–1338 s, 1295 s	1158–1140 s
$CoDEU_3I_2$	3390–3340 vs	1623 vs	1565 vs	1350–1335 s, 1295 s	1160–1140 s
$CoDEU_3(NCS)_2$	3350 vs	1625 vs	1568 vs	1348–1332 s, 1290 s	1155–1138 s
$CoDEU_6(ClO_4)_2$	3400 sh, 3330 vs, 3290 sh	1625 vs	1570 vs	1345–1330 s, 1290–1275 m	$\nu_3ClO_4^-$

TABLE VI. Magnetic Data for Ni(II) and Co(II) Compounds.

Compound	Diamagnetic Correction ($\times 10^6$)	T.I.P. Correction ($\times 10^6$)	χ_M^{corr} ($\times 10^6$)
$[NiDEU_6][NiCl_4]$	–538	240	10400
$[NiDEU_6][NiBr_4]$	–584	240	10250
$[NiDEU_6][NiI_4]$	–648	240	9300
$NiDEU_4(NCS)_2$	–358	210	4300
$NiDEU_6Br_2$	–514	240	4400
$NiDEU_6I_2$	–546	240	4300
$NiDEU_6(ClO_4)_2$	–509	240	4400
$[CoDEU_6][CoCl_4]$	–538	550	19400
$[CoDEU_6][CoBr_4]$	–584	630	18900
$[CoDEU_6][CoI_4]$	–648	840	18700
$[CoDEU_6][Co(NCS)_4]$	–568	440	17600
$CoDEU_6(ClO_4)_2$	–509	–	9800

TABLE VII. X-Ray Powder Types for $MDEU_6Y$.

Y $MDEU_6$	MCl_4	MBr_4	MI_4	Br_2	I_2	$(ClO_4)_2$
Mn	A′	B	–	D	D′	E
Co	A	C	C′	–	–	E
Ni	A	C	C′	D	D′	E

action between the octahedral and the tetrahedral cobalt(II) species can explain that difference. Therefore, a study at variable temperature is now undertaken.

Powder Diffraction Patterns

The X-ray powder diagrams are compared in Table VII.

The X-ray powder types, for the most part, are due to different anions. For the same anions, powder diagrams are almost identical except for the bromide Mn (II) compound. The interplanar distances are slightly larger for Mn(II) complexes, in agreement with the metal ion size. Moreover, the bromide and iodide compounds are isostructural but the interplanar distances are larger in the case of the iodides.

Conclusion

From the results discussed above and the previous paper[1], N,N′-diethylurea gives chiefly two kinds of compounds: $M(DEU)_6X_2$ octahedral and $M(DEU)_3X_2$ octahedral–tetrahedral that must be written as $[MDEU_6][MX_4]$. In all cases, the ligand is coordinated through the oxygen atom (IR spectra). The mixed species $[MDEU_6][MX_4]$ are clearly recognized: electronic and IR spectra appear to be the addition of those of the $[MX_4]^{2-}$ anion and the $[M(DEU)_6]^{2+}$ cation. This latter cation like a large NR_4^+ cation stabilizes the $[MX_4]^{2-}$ species. The fact that $Co(DEU)_6X_2$ with X = I or Br is not obtained, the existence of $[NiI_4]^{2-}$ and the absence of $[MnI_4]^{2-}$ indicate a decrease of stability of the $[MX_4]^{2-}$ anions *versus* $[CoX_4]^{2-}$, *via* $[NiX_4]^{2-}$ to $[MnX_4]^{2-}$ in agreement with crystal-field stabilization energies for high spin ions.

The NCS^- group is bonded through the nitrogen atom for Co(II) and Ni(II) compounds as is usually observed for the first-row transition metal ions. The molecular $Ni(DEU)_4(NCS)_2$ complex has probably an octahedral *trans* structure as most $ML_4(NCS)_2$ compounds.

Hydrogen bonding seems to be present between the N–H group of N,N′-diethylurea and the anions (X_2 or $[MX_4]^{2-}$): indeed the N–H stretching is similar in $M(DEU)_6$ Y with M = Mn, Co or Ni for the same anion Y and slightly different when the anion changes.

Whereas magnetic data for tetrahedral Ni(II) compounds agree very well with literature, those of tetrahedral Co(II) compounds are different. The largest deviation is observed for $[CoCl_4]^{2-}$, the smallest tetrahedral anion which should give the highest interaction between two kinds of cobalt(II) and explain these results.

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