CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
THE OHIO STATE UNIVERSITY, COLUMBUS, OHIO 43210

Complexes Derived from the Reaction of Hexaamminenickel(II) Ion with Acetone

BY NORMAN J. ROSE, MICHAEL S. ELDER, AND DARYLE H. BUSCH

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The properties and isomeric nature of the compounds derived from the condensation reactions of tris(ethylenediamine)nickel(II) salts with acetone are well documented and have provided unique insight into the stereochemistry of square-planar complexes.[1-4] In spite of the relatively high interest attending this and similar reactions involving polyamine nickel(II) complexes, little information is available concerning the corresponding reaction with acetone of the primordial amine complex in this series: hexaamminenickel(II).[5,6] Jehn reports the preparation of cationic complexes obtained from reactions of the hexaamminenickel(II) salts with (1) acetone in the presence of triphenyltin bromide and (2) mesityl oxide.[7] He proposes that the product contains two bidentate ligands (L) per nickel ion and that the complex ion has the structure indicated in Figure 1. Although allusion is made to supporting analytical, magnetic, and spectral data, no quantitative information of this kind is contained in his abbreviated note. The sole published support of structure is the synthesis itself, *viz.*, preparation of the complexes from mesityl oxide. We report here, in some detail, the preparation and properties of NiL_2^{2+} salts as well as an unanticipated NiL_3^{2+} salt. Besides magnetic susceptibility data, the structural inferences rest on evidence obtained from electronic, infrared, and nuclear magnetic resonance spectra.

The preparation of the $NiL_3(PF_6)_2$ is accomplished at room temperature by simply dissolving the hexaamminenickel(II) hexafluorophosphate salt in acetone. Over a period of 3 days the solution changes in color from violet to red-orange. Reduction of the solution volume followed by addition of ether affords an orange solid. The undissolved substance remaining after extraction of the orange product with methanol can be recrystallized from acetone–ether to yield violet crystals of the desired complex, $NiL_3(PF_6)_2$. The $NiL_2(PF_6)_2$ is most readily prepared in high yield by refluxing a mixture of $Ni(NH_3)_6(PF_6)_2$ and acetone for 5 hr. Reduction of the solution volume followed by addition of ether provides yellow crystals which can be purified by recrystallization from methanol–ether.

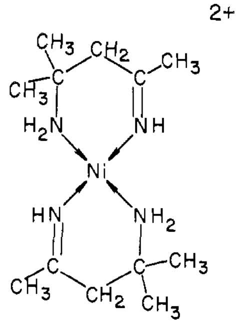

Figure 1.—Proposed structure for the Ni(II) complex derived from hexaamminenickel(II) ion and acetone.

Results and Discussion

Tables I and II contain values for the properties and analytical data for the NiL_2 and NiL_3 salts reported here. In all cases the infrared spectra of these complexes are characterized by relatively strong bands in the 3000–3333-cm^{-1} region and by a sharp, intense singlet or closely spaced doublet near 1660 cm^{-1}. Bands in the former region can be assigned to the NH_2 stretching modes of a coordinated primary amine and those of the latter region to the CN stretch of a coordinated imine function.[6,8] For each complex an absorption also occurs at or near 1600 cm^{-1}. This absorption may be attributed to the NH_2 deformation motions.[8] In addition to supporting the proposed structure of the ligand, the infrared spectra for the NiL_2 compounds present an interesting trend as a function of anion in the 3000–3333-cm^{-1} region. The average position of the absorptions in this area moves to lower energy as the anion changes from PF_6^- to $ZnCl_4^{2-}$ to I^- to Br^- to Cl^-. This result is taken as evidence for the hydrogen bonding of the anions with the protons of the amine nitrogen. Both in direction of frequency shift and in order of anions, the reported trend is precisely that expected with the most electronegative group, Cl^-, showing the strongest interaction (lowest frequency) and the least electronegative anion, PF_6^-, showing the weakest interaction (highest frequency). Similar anion dependencies of the NH stretching frequencies have been observed for ammonia and for ethylenediamine complexes; these dependencies also have been attributed to hydrogen bonding.[9,10]

The only two anions having absorptions in the infrared region investigated are PF_6^- and NCS^-. Wherever the former ion is present, the expected strong bands appear at 850 and 560 cm^{-1}.[11] The strong peak present at 2088 cm^{-1} for the NCS^- complex may be assigned to the CN stretching mode for that anion. The specific position of this band suggests that the nickel ion is coordinated to the nitrogen rather than to the sulfur atom of the NCS^-.[12] The positions of the other NCS^- vibrations (the NCS^- deformation and the CS stretch) are of known diagnostic use in distinguishing

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TABLE I

PROPERTIES AND ANALYSIS FOR 4-METHYL-4-AMINO-2-IMINOPENTANENICKEL(II) SALTS

Complex	% C Calcd	% C Found	% H Calcd	% H Found	% N Calcd	% N Found		% other Calcd	% other Found	μ_{eff}, BM
NiL_2Cl_2	40.26	40.22	7.88	7.92	15.65	15.80	Cl	19.81	19.74	0.3
NiL_2Br_2	32.24	32.31	6.31	6.23	12.54	12.63	Br	35.76	35.68	
NiL_2I_2	26.64	26.72	5.22	5.19	10.36	10.25	I	46.88	46.76	
$NiL_2(PF_6)_2$	24.98	25.01	4.89	4.90	9.71	9.62	F	39.51	39.88	
NiL_2ZnCl_4	29.16	29.08	5.71	5.70	11.34	11.22	Cl	28.69	28.66	
$NiL_2(NCS)_2$	41.70	41.71	7.00	7.00	20.85	20.80	S	15.90	15.84	3.07, 3.09
$NiL_3(PF_6)_2$	31.28	31.38	6.13	6.09	12.17	11.83	F	32.99	33.12	3.08

TABLE II

INFRARED AND ELECTRONIC SPECTRA FOR 4-METHYL-4-AMINO-2-IMINOPENTANENICKEL(II) SALTS[a]

Complex	NH and NH_2 str, cm^{-1}	CN str, cm^{-1}	NH_2 def, cm^{-1}	Anion modes, cm^{-1}	ν(max), cm^{-1}
NiL_2Cl_2	3170 s 3130 s 3015 s	1650 s	1600 w 1585 w		23,600
NiL_2Br_2	3168 s 3142 s 3105 s 3030 s	1650 s	1610 w 1585 w		23,300
NiL_2I_2	3175 s 3152 s 3070 s	1650 s	1585 m		22,900
NiL_2ZnCl_4	3218 s 3115 s	1655 s	1590 m[b]		23,000
$NiL_2(PF_6)_2$	3332 s 3278 s 3175 w	1660 s[b]	1600 s	850 s 560 s	23,250
$NiL_3(PF_6)_2$	3333 s 3311 s 3155 w	1655 s	1590 s[b]	850 s 560 s	11,400[c] 18,700
$NiL_2(NCS)_2$	3311 m 3236 s 3145 m	1660 s[b]	1590 s	2088 s[d]	10,700 18,700

[a] All spectra obtained as Nujol mulls: s, strong; m, medium; w, weak. [b] Peak is closely spaced doublet. [c] A very weak band appears as a shoulder at ~12,700 cm^{-1}. [d] CN stretch of NCS^-.

between N and S bonding but are not readily identified for this particular NCS^- complex.[12,13]

Nuclear magnetic resonance studies at 35° of the $NiL_2(PF_6)_2$ compound in deuterated acetone provide strong corroborating evidence for the structure of the ligand. There are two resonances assignable to the methyl protons of the ligand, one at 1.70 ppm (relative intensity 6) and the other at 2.21 ppm (relative intensity 2.97) downfield from internal TMS. The intensity ratio of 2:1 permits the unequivocal assignment of the 1.70-ppm resonance to the protons of the geminal methyl groups on the carbon adjacent to the primary amine and of the 2.21-ppm resonance to the protons of the methyl group on the imine carbon. Unlike the corresponding complex derived from ethylenediamine and acetone, the geminal methyl groups cannot be distinguished at 35° even though both complexes contain the same six-membered chelate ring.[1] The barrier to flexing of these rings imposed by the presence of the bridging ethylenic units of the former complex is therefore unmistakenly indicated. The remaining resonance of the $NiL_2(PF_6)_2$ complex occurs at 2.72 ppm (relative intensity 2.26) and can be assigned to the methylenic protons. The relative intensity for this peak is greater than the expected value, 2, by a factor in excess of experimental error. The excessive value can be attributed to a contribution to the intensity from broad resonances assignable to the protons on the nitrogen atoms of the complex. The broad nature of the resonances due to the protons bound to nitrogen is supported by the absence of any identifiable peaks between the assigned methylenic resonance (2.72 ppm) and 4.97 ppm.

The NiL_2^{2+} complexes of chloride, bromide, iodide, tetrachlorozincate, and hexafluorophosphate all have similar electronic spectra in that each shows a single band in the 23,000-cm^{-1} spectral region (Table II). These data coupled with the spin-paired nature of the chloride salt (Table I) are consistent with assigning these complexes a square-planar structure.[14] No evidence is presently available which permits distinguishing a *trans*- from a *cis*-imine arrangement.

The $NiL_2(NCS)_2$ and the $NiL_3(PF_6)_2$ compounds are spin-free octahedral complexes as indicated both by their effective magnetic moments (Table I) and by their electronic spectra (Table II). The measured magnetic moment of 3.08 BM (for both complexes) is well within the range expected for six-coordinate nickel(II). Of the two electronic transitions observed in each case, the band at the lower energy can be assigned to ${}^3T_{2g}(F) \leftarrow {}^3A_{2g}(F)$ and the one at higher energy to ${}^3T_{1g}(F) \leftarrow {}^3A_{2g}(F)$.[14] It is presumed that the third transition usually found for octahedral or pseudo-octahedral nickel(II) complexes is obscured by the very intense band centered beyond 31,000 cm^{-1} which is found in the spectra of both complexes considered here. The shoulder which appears on the 11,400-cm^{-1} transition of the NiL_3^{2+} salt can be attributed to a spin-forbidden triplet to singlet transition as is a similar shoulder noted in the spectrum of the tris(trimethylenediamine)nickel(II) complex.[15]

The average ligand fields for these six-coordinate complexes follow the pattern empirically derived from the electronic spectra of similar nickel(II) species. Thus, in the five-membered chelate ring, the substitution of an imine nitrogen for one of the amine nitrogen atoms causes a change in *Dq* value from 1120 to 1160 cm^{-1} (Table III).[16] A similar elevation is noted

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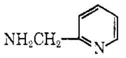
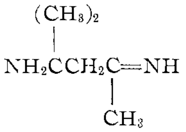
in the six-membered ring systems reported here compared to the parent alkyldiamine, trimethylenediamine. In this case the change is from 1090 to 1140 cm^{-1} (Table III). The replacement of one ligand (L) by two NCS$^-$ groups causes an expected lowering of the Dq value (to 1070 cm^{-1}) in that NCS$^-$ is found below both amine and imine donors in the spectrochemical series.[14]

Table III

Dq Values for NiB_3^{2+} Species

B	Dq, cm^{-1}	Ref
$NH_2CH_2CH_2NH_2$	1120	14
	1160^a 1190^b	16
$NH_2CH_2CH_2CH_2NH_2$	1090	15
 $NH_2\overset{(CH_3)_2}{\overset{\vert}{C}}CH_2\underset{\underset{CH_3}{\vert}}{C}{=}NH$	1140	This work

^{a} Purple isomer. ^{b} Brown isomer.

Experimental Section

The reagents used as starting materials were obtained commercially and employed without further purification. Unless otherwise indicated, the products were all dried at room temperature for 14 hr over P_4O_{10} at 1 mm.

Hexaamminenickel(II) Hexafluorophosphate.—A procedure similar to that employed by Lange and Müller was adopted.[17] To a solution of $Ni(OAc)_2\cdot 4H_2O$ (2.39 g, 9.6 mmoles) in 60 ml of 15 *M* NH_4OH was added a filtered solution of NH_4PF_6 (2.6 g, 16 mmoles) in 40 ml of water. The resulting violet precipitate was collected on a suction filter and washed in order with 15 *M* NH_4OH, ethanol, and ether. Drying was achieved by passing anhydrous air through the sample for about 1 hr. *Anal.* Calcd for $Ni(NH_3)_6(PF_6)_2$: N, 18.64. Found: N, 18.74.

Hexaamminenickel(II) Bromide.—A warm solution of $NiBr_2\cdot 3H_2O$ (5 g, 18.3 mmoles) was added to 60 ml of warm 15 *M* NH_4OH. The resulting violet precipitate was collected, washed, and dried as indicated in the preceding preparation. *Anal.* Calcd for $Ni(NH_3)_6Br_2$: N, 26.20. Found: N, 25.92.

Tris(4-methyl-4-amino-2-iminopentane)nickel(II) Hexafluorophosphate.—During the course of this preparation all reagents and solutions were maintained at room temperature or below. A mixture of $Ni(NH_3)_6(PF_6)_2$ (2.57 g, 5.7 mmoles) and 150 ml of acetone was allowed to stand at room temperature for 3 days. Reduction of the solution volume to 30 ml followed by the addition of 200 ml of ether resulted in the formation of an orange solid. The pink undissolved portion of this orange solid, remaining after extraction with 30 ml of methanol, was crystallized from acetone and ether by first dissolving the pink solid in 30 ml of acetone and then adding ether to incipient cloudiness. Filtration of the cloudy solution followed by cooling to about 5° afforded crystals which were collected and washed with ether; yield, 0.33 g (8%).

Bis(4-methyl-4-amino-2-iminopentane)nickel(II) Hexafluorophosphate.—A mixture of $Ni(NH_3)_6(PF_6)_3$ (2.79 g, 6.2 mmoles) and 300 ml of acetone was refluxed for 5 hr and then allowed to stand at room temperature for 16 hr. After the resulting clear orange liquid had been reduced to approximately one-fifth its original volume, ether was added until the precipitation of yellow crystals was complete; yield, 2.89 g. The yellow crystals were purified by first dissolving them in methanol (room temperature) and then adding ether to incipient cloudiness. Filtration followed by cooling to about 5° resulted in the formation of crystals which were collected and washed with ether.

Bis(4-methyl-4-amino-2-iminopentane)nickel(II) Bromide.—A mixture of 200 ml of methanol, 50 ml of acetone, $Ni(NH_3)_6Br_2$ (4.6 g, 14.4 mmoles), and $NiBr_2\cdot 3H_2O$ (1.9 g, 7 mmoles) was stirred at room temperature for 4 days. The resulting yellow-green solid was collected (4.26 g) and extracted with 450 ml of methanol at room temperature. To the filtrate of this extraction was added ether to the point of incipient cloudiness. Filtration of this cloudy solution followed by cooling to about 0° resulted in the formation of needle crystals which were collected and washed with a mixture of methanol and ether (1:1 by volume). The extraction and crystallization were repeated starting with 300 ml of methanol.

Bis(4-methyl-4-amino-2-iminopentane)nickel(III) Chloride.—The following procedure was done at room temperature. To a filtered solution of acetone (60 ml) saturated with LiCl was added a filtered solution of acetone (5 ml) containing $NiL_2(PF_6)_2$ (0.2 g, 0.35 mmole). The yellow crystals that separated were collected and washed with acetone; yield, 0.04 g (32%).

Bis(4-methyl-4-amino-2-iminopentane)nickel(II) Tetrachlorozincate.—The following procedure was done at room temperature. A filtered solution of methanol (15 ml) containing NiL_2Cl_2 (0.47 g, 1.3 mmoles) was added to a filtered solution of methanol (15 ml) containing $ZnCl_2$ (0.18 g, 1.3 mmoles). The yellow crystals that separated were washed with methanol after being collected; yield, 0.37 g (58%).

Bis(4-methyl-4-amino-2-iminopentane)nickel(II) Iodide.—The following procedure was done at room temperature. To a filtered solution of acetone (40 ml) containing NaI (0.5 g, 3.3 mmoles) was added a filtered solution of acetone (20 ml) containing $NiL_2(PF_6)_2$ (0.69 g, 1.2 mmoles). The yellow crystals that separated were collected and washed with acetone; yield, 0.49 g (76%).

Bisthiocyanatobis(4-methyl-4-amino-2-iminopentane)nickel(II). The following procedure was done at room temperature. A filtered solution of acetone (10 ml) containing NaSCN (0.16 g, 2 mmoles) was added to a filtered solution of acetone (10 ml) containing $NiL_2(PF_6)_2$ (0.57 g, 1 mmole). Ether was added to incipient cloudiness. Upon standing, the solution deposited violet crystals which were collected and washed with ether; yield, 0.27 g (67%).

Physical Measurements.—Infrared spectra were determined in Nujol mulls with a Perkin-Elmer 337 or Beckman IR-9 recording spectrophotometer. A Cary Model 14 spectrophotometer was used for measurements in the ultraviolet, visible, and near-infrared spectral ranges. Magnetic susceptibility data were obtained at 22° by the Faraday technique.

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Contribution from the Department of Chemistry,
University of Nottingham, Nottingham, England

The Reaction of Dirhenium Decacarbonyl with Dinitrogen Tetroxide. Nitratopentacarbonylrhenium(I)

By C. C. Addison, R. Davis, and N. Logan

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Reactions of excess liquid dinitrogen tetroxide with the hexacarbonyls of chromium,[1] molybdenum, and

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