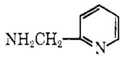
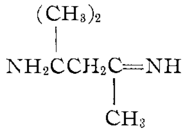
in the six-membered ring systems reported here compared to the parent alkyldiamine, trimethylenediamine. In this case the change is from 1090 to 1140 cm^{-1} (Table III). The replacement of one ligand (L) by two NCS$^-$ groups causes an expected lowering of the Dq value (to 1070 cm^{-1}) in that NCS$^-$ 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
 $NH_2C(CH_3)_2CH_2C(CH_3){=}NH$	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,
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The Reaction of Dirhenium Decacarbonyl with Dinitrogen Tetroxide. Nitratopentacarbonylrhenium(I)

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

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[1] C. C. Addison and D. J. Chapman, *J. Chem. Soc.*, 539 (1964).

tungsten,[2] dimanganese decacarbonyl,[3] iron pentacarbonyl,[4] dicobalt octacarbonyl,[5] and nickel tetracarbonyl[6] result in complete removal of carbonyl groups. The compatibility of nitrate and carbonyl ligands has, nevertheless, been demonstrated by the preparation of the compound nitratopentacarbonylmanganese(I), $Mn(CO)_5NO_3$. However, reaction of dimanganese decacarbonyl with excess dinitrogen tetroxide in petroleum ether (bp 40–60°) gives rise to a mixture of products,[3] the principal constituents being nitrato- and nitropentacarbonylmanganese(I). A rather complicated extraction and fractional crystallization procedure is then necessary for the isolation of the pure nitrato complex, which is involatile.

In contrast, the reaction of dirhenium decacarbonyl with excess liquid dinitrogen tetroxide (alone or mixed with acetonitrile) leads directly to the production of nitratopentacarbonylrhenium(I), presumably according to the equation $Re_2(CO)_{10} + 2N_2O_4 \rightarrow 2Re(CO)_5NO_3 + 2NO$. This product can be purified by vacuum sublimation at 100°.

Experimental Section

Dirhenium decacarbonyl was obtained from Strem Chemicals Inc. and used without further purification. Liquid dinitrogen tetroxide was prepared and purified as described elsewhere.[7] All organic solvents were dried and purified by standard techniques.

Infrared spectra were recorded on a Perkin-Elmer 521 grating spectrophotometer as mulls in Nujol and Halocarbon oil, using polythene-protected cesium iodide windows.

Carbon content was determined by a "wet-combustion" method. The material was oxidized in a closed system with a mixture of chromic oxide, phosphoric acid, fuming sulfuric acid, and potassium iodate. The carbon dioxide produced was determined by absorption.[8] Rhenium was determined by vigorous oxidation with 70% perchloric acid to perrhenate which was estimated by the method of Headridge.[9] Nitrogen was determined by the Dumas method.

Preparation of $Re(CO)_5NO_3$.—Liquid dinitrogen tetroxide (10 ml) was added to dirhenium decacarbonyl (1 g) at 0° in a vessel vented to the atmosphere through phosphoric oxide. On warming slowly to 20°, the carbonyl dissolved to give a green N_2O_3 solution which was shaken for 3 hr at this temperature; no precipitation occurred. On removal of the nitrogen oxides under vacuum at 20°, a buff-colored powder remained. *Anal.* Found: Re, 43.8; C, 16.4. On heating this powder to 100° under vacuum, a white crystalline sublimate was obtained. *Anal.* Calcd for $Re(CO)_5NO_3$: Re, 47.9; C, 15.5; N, 3.61. Found: Re, 47.5; C, 15.3; N, 3.75; 70% yield based on $Re_2(CO)_{10}$. The same reaction, using a mixture of dinitrogen tetroxide and acetonitrile, gave an identical product, so that the course of the reaction is apparently unaffected by a cosolvent having a high dielectric constant and appreciable electron pair donating ability.

Results and Discussion

Nitratopentacarbonylrhenium(I) is a white crystalline solid which is indefinitely stable, even in moist air. At atmospheric pressure, it decomposes without melting at 125–130°. The compound is soluble in most polar solvents and can be recrystallized from methanol. It is insoluble in water, benzene, cyclohexane, petroleum ether, carbon tetrachloride, *sym*-tetrachloroethane, and carbon disulfide. Cryoscopic measurements of molecular weight in nitrobenzene gave values of 260 (0.0125 M) and 281 (0.0200 M) indicating appreciable dissociation of the nitratocarbonyl at these concentrations (calcd for $Re(CO)_5NO_3$: 388). This may well be due to solvent coordination with release of ionic nitrate groups, as occurs with some derivatives of $Mn(CO)_5NO_3$.[10] The compound is diamagnetic (χ_m at 24° by the Gouy method is -243.9×10^{-6} cgs unit) as expected for Re(I). The infrared spectrum of nitratopentacarbonylrhenium(I) shows a marked similarity to those of the rhenium pentacarbonyl halides in the carbonyl stretching region,[11] the M–C–O deformation region, and the M–C stretching region,[12] confirming the presence of octahedrally coordinated Re(I). The nitrate bands in the spectrum of $Re(CO)_5NO_3$ are simple and clearly defined and are closely analogous to those of nitratopentacarbonylmanganese(I)[3] in which nitrate coordination is considered to be unidentate.

A detailed examination of the solution properties, the Raman spectrum, and the X-ray crystallography of $Re(CO)_5NO_3$ is in progress. The crystallography is particularly important since no truly unidentate nitrate group has yet been confirmed by this method.

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The Preparation of Sodium Tris(2,2′-bipyridine)ferrate(−I)[1]

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A number of 2,2′-bipyridine complexes with metals in low oxidation states, including tris(2,2′-bipyridine)iron(0), have been reported in recent years.[2–5] In this note we report the preparation of sodium tris(2,2′-bipyridine)ferrate(−I).

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