$(NH_3)_4C_2O_4^+$ and $Co(en)_2C_2O_4^+$ ions.[14] The correctness of the conclusion that the oxalate in $Rh(en)_2C_2O_4^+$ is chelated therefore seems assured.

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Complexes of Aziridine with Nickel(II) Chloride

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Reports on the complexes of aziridine with transition metal ions have appeared since 1961.[1–4] We have undertaken an investigation of the coordinating properties of the three-membered heterocycle as it occurs in aziridine and its *N*-aminoalkyl derivatives which are capable of chelate ring formation. The potential for ring-opening reactions of the coordinated aziridine ring is also under investigation.

Complexes of the type $[Ni(Az)_6]X_2$ (Az = aziridine, $X^- = NO_3^-, Br^-, I^-$) have been reported by Jackson and Edwards.[1] The previously unreported chloride salt has been prepared by the reaction of anhydrous nickel(II) chloride directly with aziridine. The use of a solvent leads to the formation of $Ni(Az)_4Cl_2$ which has been reported but not completely characterized.[1] The violet hexaaziridinenickel(II) chloride, $[Ni(Az)_6]Cl_2$, has absorption bands at 17,100, 27,400, and 42,000 cm^{-1} in the solid state in agreement with the published spectrum of the nitrate salt in solution.[3] The $^3A_{2g} \rightarrow {}^3T_{2g}$ transition could not be observed due to decomposition of the sample by the heat of the infrared source of the spectrophotometer.

The light blue complex $Ni(Az)_4Cl_2$ can be prepared either by the reaction of nickel(II) chloride and aziridine in methanol or by the thermal decomposition of $[Ni(Az)_6]Cl_2$ at 56° and about 5 Torr. At room temperature there is only a suggestion of the splitting in the electronic spectrum which is observed clearly at liquid nitrogen temperature.[5] Bands at 8375, 11,890, 12,800, 13,870, 17,150, and 27,200 cm^{-1} were assigned to the transitions from the ground $^3B_{1g}$ state to ^3E_g, $^3B_{2g}$, $(^1A_{1g}, {}^1B_{1g})$, $^3A_{2g}(^3F)$, $^3E_g(^3F)$, and $^3E_g(^3P)$, respectively, assuming D_{4h} symmetry. On the basis of the magnitude of the splitting observed and the similarity of the spectrum to those of complexes of known structure, the assignment of the trans geometric configuration is made.[5] No evidence of isomerization has been observed. The measured magnetic moment of 3.09 BM supports the assignment of a six-coordinate structure.

By the thermal decomposition of $[Ni(Az)_6]Cl_2$ or $Ni(Az)_4Cl_2$ at 100° *in vacuo*, we have prepared $Ni(Az)_2Cl_2$. This pale green solid could not be prepared by wet chemical methods. In the spectrum of $Ni(Az)_2Cl_2$ run at liquid nitrogen temperature,[6] maxima were observed at ~7840 (broad and structured), ~9760, 12,700, 14,700, 19,900, and 24,500 cm^{-1}. The position and relative intensities of these absorption maxima and the magnetic moment of 3.19 BM support assignment of a six-coordinate structure. It is likely that a chloride-bridged polymeric structure similar to that shown to exist for $Ni(py)_2Cl_2$ is assumed by this material.[7,8] The similarity of the electronic spectrum of $Ni(Az)_2Cl_2$ to that of $Ni(py)_2Cl_2$ at liquid nitrogen temperature[6] supports this hypothesis though the lack of quantitative agreement with a tetragonal model having a strong axial field suggests that some other six-coordinate structure might be assumed. It is noted that several diamines of stoichiometry $Ni(diamine)Cl_2$ also appear to have six-coordinate polymeric structures.[9]

TABLE I

ANALYTICAL AND MAGNETIC RESULTS FOR AZIRIDINE COMPLEXES OF NICKEL(II) CHLORIDE

		Analyses, %								
		Calcd				Found				
Compound	Color	C	H	N	Cl	C	H	N	Cl	μ_{eff}, BM
$[Ni(Az)_6]Cl_2$	Violet	37.14	7.79	21.66	18.27	36.59	7.80	19.91	18.77	3.22
$Ni(Az)_4Cl_2$	Blue	31.83	6.68	18.56	23.49	31.52	6.68	18.31	23.39	3.09
$Ni(Az)_2Cl_2$	Green	22.22	4.67	12.98	32.86	22.33	4.97	12.96	32.58	3.19

For all three complexes a strong absorption occurs between 870 and 900 cm^{-1}. This band is attributed to deformation of the aziridine ring. A band in the 3370–3450-cm^{-1} region is also present and is assigned to the N-H stretching mode of the coordinated aziridine.

The interconversions of compounds of aziridine with nickel(II) chloride are illustrated by

$$\begin{tikzcd}
Ni(Az)_4Cl_2 \arrow[rr, shift left, "Az"] \arrow[dr, shift left, "\Delta"] & & {[Ni(Az)_6]Cl_2} \arrow[ll, shift left, "\Delta"] \arrow[dl, shift left, "\Delta"'] \\
& Ni(Az)_2Cl_2 \arrow[ul, shift left, "\begin{array}{l}Az\\ \text{in } C_2H_5OH\end{array}"] \arrow[ur, shift left, "Az"'] &
\end{tikzcd}$$

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Experimental Section

Analyses were performed by Galbraith Laboratories, Inc. The compounds rich in aziridine presented some difficulty in handling since aziridine is readily sublimed from the sample under normal room conditions.

The thermal decompositions were run in an Abderhalden condenser. Decomposition was continued until the sample weight became constant.

Magnetic moments were determined by the Gouy method using mercuric tetrathiocyanatocobaltate(II) as standard. Diamagnetic corrections were made using Pascal's constants.

Electronic absorption spectra were recorded with a Cary 14 spectrophotometer. Absorption of solids was measured with Nujol mulls on filter paper.

All chemicals were of reagent grade. Aziridine was supplied by Dow Chemical Co., Midland, Mich.

Hexaaziridinenickel(II) Chloride, $[Ni(Az)_6]Cl_2$.—A heterogeneous reaction between aziridine and anhydrous nickel(II) chloride is run in a beaker surrounded by ice. The resulting violet mass is treated with dry ether to improve the physical form and filtered. After several washings with dry ether, the solid product is dried in a desiccator over KOH pellets. Care must be taken in handling this compound because it readily loses aziridine on standing. It was difficult to obtain satisfactory analytical data for this reason. $[Ni(Az)_6]Cl_2$ can also be prepared by the direct reaction of aziridine with $Ni(Az)_4Cl_2$ or $Ni(Az)_2Cl_2$.

Dichlorotetraaziridinenickel(II), $Ni(Az)_4Cl_2$.—To a solution of hydrated nickel(II) chloride in methanol, an excess of aziridine is added. The addition is made at ice bath temperature with stirring, producing a deep blue color. Slow addition of a small amount of ether causes precipitation of the blue product which is isolated by filtration and dried in a desiccator over KOH pellets. $Ni(Az)_4Cl_2$ can also be prepared by dissolving $Ni(Az)_2Cl_2$ in an ethanol solution of aziridine and isolating the product in the same manner described above.

Dichlorodiaziridinenickel(II), $Ni(Az)_2Cl_2$.—$Ni(Az)_2Cl_2$ is prepared by the thermal decomposition of $[Ni(Az)_6]Cl_2$ or $Ni(Az)_4Cl_2$ in an Abderhalden apparatus at 100° and a pressure of approximately 5 Torr. All attempts to prepare this compound directly from nickel(II) chloride have been unsuccessful.

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Preparation and Reactivity of New Azido-Bridged Complexes of Rhodium(I)

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Although azido-bridged complexes have been presumed by several authors,[1-4] it is recently that such complexes have been fully characterized.[5-7]

This paper reports the preparation of new Rh^I azido-bridged complexes by a general method which can be extended to the synthesis of analogous transition metal complexes.

Experimental Section

Materials.—The compounds $[(CO)_2RhCl]_2$,[8] $[C_8H_{12}RhCl]_2$,[9] $[C_{10}H_{12}RhCl]_2$,[9] $[C_7H_8RhCl]_2$,[10] $[C_8H_8RhCl]_2$,[11] and $[(P(C_6H_5)_3)_2RhCl]_2$[12] were synthesized as described in the literature. Tetrabutylammonium azide was prepared as described by Gutmann.[13] Absolute methanol was dried and purified by distillation after refluxing over $Mg(OCH_3)_2$. All the chemicals used were reagent grade.

Preparation of $[(CO)_2RhN_3]_2$.—To a stirred suspension of 0.388 g (1 mmol) of $[(CO)_2RhCl]_2$ in 20 ml of dry methanol, 0.140 g (2.15 mmol) of sodium azide was added in a nitrogen atmosphere at room temperature. Immediately the solution turned yellow-brown while a deep red precipitate was formed. After 1 hr the solution was filtered and the dimeric compound was recrystallized from dichloromethane–methanol. The yield was almost quantitative (mp 120–125° dec). The compound is air stable in the solid state, although it decomposes in solution to a dark insoluble solid (probably a polymeric form). The complex $[(CO)_2RhN_3]_2$ is soluble in CH_2Cl_2 and $CHCl_3$, slightly soluble in methanol, and insoluble in hydrocarbons.

Preparation of $[(diene)RhN_3]_2$.—These complexes were prepared in an almost quantitative yield by the following procedure.

To a suspension of 0.1 mmol of $[(diene)RhCl]_2$ in dry methanol a twofold molar excess of solid NaN_3 was added with stirring in a nitrogen atmosphere. After 4–5 hr the reaction mixture was filtered and washed with a few milliliters of water to remove the excess of sodium azide, methanol, and ether. All the complexes prepared with the procedure described above were recrystallized from dichloromethane–hexane. Analytical data and physical properties of $[(diene)RhN_3]_2$ are reported in Table I.

Preparation of $(P(C_6H_5)_3)_2Rh(CO)N_3$.—A solution of 0.200 g (0.5 mmol) of $[(CO)_2RhN_3]_2$ in CH_2Cl_2 was treated with an excess of triphenylphosphine (0.500 g) in a nitrogen atmosphere. After a few minutes the solution turned from orange-yellow to pale yellow, and after 20 min the solvent was removed leaving a yellow solid which was washed several times with hexane and crystallized from CH_2Cl_2–hexane.

Its ir spectrum and physical properties are identical with those of the compound prepared according to the literature procedure by metathesis from $(P(C_6H_5)_3)_2Rh(CO)Cl$ and $N(C_2H_5)_4N_3$.[14,15]

Preparation of $(diene)Rh(P(C_6H_5)_3)N_3$.—A stirred suspension of 0.100 g $[(diene)RhN_3]_2$ (diene = C_7H_8, C_8H_{12}, $C_{10}H_{12}$) in petroleum ether (bp 40–60°) was treated dropwise with a petroleum ether solution containing the stoichiometric amount of triphenylphosphine. After 10 hr the mixture was filtered and the yellow residue was washed with hexane. The complexes $(diene)Rh(P(C_6H_5)_3N_3$ were characterized by their elemental analysis and ir spectra (see Tables I and II).

Reactions of Azido-Bridged Complexes with Carbon Monoxide.—When carbon monoxide was bubbled through a CH_2Cl_2 solution of $[(CO)_2RhN_3]_2$ or $[(diene)RhN_3]_2$ for 24 hr at room temperature, the complex $[(CO)_2Rh(NCO)]_2$ was obtained in both cases, after evaporation of the solvent and recrystallization from CH_2Cl_2–pentane. The red $[(CO)_2Rh(NCO)]_2$ complex melts with decomposition at 170–175° and is stable in air in the solid state but decomposes very slowly in solution. It dissolves in chlo-

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