was not detectable. If the oxygen atom of adenosine N_1-oxide was the binding site, the value of $^4J_{\mathrm{PtON_1C_2H_2}}$ should be smaller than $^3J_{\mathrm{PtN_1C_2H_2}}$ (22 Hz for adenosine) or not detectable at all. We found a coupling constant of 24 Hz in this complex and the possibility of assigning this large coupling constant to $^4J_{\mathrm{PtON_1C_2H_2}}$ must be ruled out.

To our knowledge, no purine ribosides studied to date have been found to coordinate through N_3. If we consider N_3 as a binding site, in addition to N_1 and N_7, then the coupling constant of H_2 should be of the order of 45 Hz, as it was found in the case of purine riboside for H_6. The chemical shift also should be significantly changed due to the presence of the platinum atoms at N_1 and N_3. This was not observed. Furthermore, molecular models show that if N_3 was coordinated to platinum, H_1' of the sugar group comes close to it and should, therefore, show coupling.[9] In this conformation, the H_1' is directed toward the square plane of the platinum complex and should have a significant coupling with ^{195}Pt. It is shown in Figures 1-3 (bottom) that H_1' gives a doublet as a result of coupling with H_2', which is the same as in the free ligand. No platinum-195 satellites were observed. Therefore, the possibility of N_3 coordination is ruled out.

Cytidine. The nmr spectra of cytidine in D_2O have been reported.[15] The H_6 is a downfield doublet and the H_5 an upfield doublet close to the doublet of H_1'. On complexation, both H_5 and H_6 moved downfield slightly and the H_5 peaks were well separated from those of H_1', as shown in Figure 6. The spectrum consists of platinum-195 satellites at the left side of H_5. This weak signal is not the spinning peak of H_2O. It is assigned to $^4J_{\mathrm{Pt-H_5}} = 8$ Hz, which is close to $^4J_{\mathrm{Pt-H_m}}$ of pyridine complexes (H_m' meta proton of pyridine).[10] The value of $^5J_{\mathrm{Pt-H_6}}$ is too small to measure. The above results show that the platinum atom is closer to H_5 than to H_6. Both cytidine and cytosine bind to Zn(II) and Cu(II) at N_3.[5,11,13] These findings led us to conclude that N_3 of cytidine is the binding site for platinum.

Uridine. On mixing [Pt(dien)Cl]Cl with uridine, the H_5, H_6, and H_1' resonances remained unchanged. It is evident that uridine does not coordinate to platinum under these conditions. It has been reported that uridine did not bind to Zn(II)[5] and Hg(II),[7] and also thymidine did not bind to Cu(II).[11] Platinum seems to follow the trend.

Experimental Section

The nuclear magnetic resonance spectra were obtained on a Varian 60 spectrometer in D_2O solutions using DSS as an internal reference. The nucleosides were purchased from Raylo Chem. Ltd., and the ethylenetriamine complexes, [Pt(dien)Cl]Cl, were prepared following the method of Mann.[16]

Preparation of Deuterio Derivatives. For the 8-deuterioadenosine and 8-deuterio-6-methylaminepurine riboside, 0.3–0.5 g of nucleoside was dissolved in 15 ml of D_2O at 60–70° and was left for 2 days (if the temperature was higher, the standing time was shorter[17]). The solution was then evaporated to dryness under reduced pressure at 0°. 100% deuteration of H_8 was indicated from the nmr spectra.

Preparation of Solutions. In general the ligand and the platinum complex solutions were 0.1 *M* in D_2O (pH 7.50). In those cases where a large excess of the platinum complex [Pt(dien)Cl]Cl was used, this was added directly into an nmr tube which contained 0.1 *M* solution of both ligand and [Pt(dien)Cl]Cl; no correction was made for the small change in volume. In those cases where the ligand was not very soluble in D_2O, the suspension was heated at 50–60° until all of the ligand had dissolved.

Registry No. Pt, 7440-06-4; adenosine, 58-61-7; purine riboside, 550-33-4; 6-methylaminopurine riboside, 1867-73-8; adenosine N_1-oxide, 146-92-9; cytidine, 65-46-3.

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Synthesis and Characterization of 1,8-Naphthyridine Complexes of 1.5-Valent Nickel

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The bidentate ligand 1,8-naphthyridine (napy) reacts with nickel(II) salts to form not only nickel(II) complexes but also to form a series of dimeric complexes of the general formula $[Ni_2(napy)_4X_2]Y$ (X = halogen, NCS, NO_3; Y = PF_6, $B(C_6H_5)_4$) in which the nickel has a formal oxidation number of +1.5. A single-crystal X-ray structural analysis of the complex $[Ni_2(napy)_4Br_2]B(C_6H_5)_4$ was performed on the basis of 2402 independent reflections collected by a PW 1100 diffractometer. The compound crystallizes with four formula units in a monoclinic cell of symmetry $P2_1/c$ and dimensions $a = 9.931$ Å, $b = 32.311$ Å, $c = 16.535$ Å, and $\beta = 101.5°$. The structure was solved by a combination of Patterson and direct methods and refined by the full-matrix least-squares method to $R(F) = 0.077$ and $R_w(F) = 0.085$. The structure consists of binuclear cations $[Ni_2(napy)_4Br_2]^+$ and tetraphenylborate anions $B(C_6H_5)_4^-$. The coordination polyhedron consists of a distorted bicapped prism in which each nickel atom is bound to four nitrogen atoms of four napy molecules. The four nitrogen atoms lie in a plane about the nickel and the bromine at the apex. Each napy molecule acts as a bridge linking together two nickel atoms, the nickel atoms in each unit being 2.41 Å apart. The magnetic and spectral electronic properties of the compounds are discussed. The electronic spectrum of the $[Ni_2(napy)_4Br_2]B(C_6H_5)_4$ complex is discussed on the basis of single-crystal polarized data.

In recent years the coordinating properties of the ligand 1,8-naphthyridine (napy) have been the subject of many investigations.[1] A range of complexes of napy with both transition and nontransition metals have been characterized.

Generally napy has been found to function as a bidentate ligand toward single metal atoms forming complexes with coordination numbers of 6 and 8.[1a] Recently a case has been reported for napy acting as monodentate.[1b]

We have studied the complexing properties of napy and of its 4-methyl derivative (menapy) toward nickel salts in solvents of low dissociating power (*e.g.*, ethanol, butanol) and have isolated bivalent nickel complexes of the general for-

Table I. Analytical Data for napy[a] and menapy[b] Complexes of Nickel

Compd	% calcd				% found			
	C	H	N	Ni	C	H	N	Ni
$Ni(C_8H_6N_2)_2Br_2$	40.13	2.52	11.70	12.26	40.00	2.50	11.95	12.10
$Ni(C_8H_6N_2)_2I_2$	34.00	2.10	9.71	10.24	34.10	2.16	9.80	10.31
$Ni(C_9H_8N_2)_2Br_2$	42.65	3.18	11.01	11.58	42.36	3.21	11.11	11.39
$Ni(C_9H_8N_2)_2(NCS)_2$	51.85	3.47	18.10	12.67	51.92	3.53	18.46	12.66
$Ni(C_8H_6N_2)ClB(C_6H_5)_4$	71.30	4.78	8.31	8.71	70.43	4.86	7.89	8.40
$Ni(C_8H_6N_2)_2BrB(C_6H_5)_4$	66.89	4.49	7.80	8.17	66.30	4.44	7.81	8.12
$Ni_2(C_8H_6N_2)_4Cl_2B(C_6H_5)_4$	65.41	4.31	10.89	11.41	65.33	4.88	10.20	11.39
$Ni_2(C_8H_6N_2)_4Br_2B(C_6H_5)_4$	60.21	3.97	10.03	10.50	60.07	4.10	10.15	10.20
$Ni_2(C_8H_6N_2)_4I_2B(C_6H_5)_4$	55.53	3.66	9.25	9.69	55.11	3.58	9.16	9.58
$Ni_2(C_8H_6N_2)_4(NO_3)_2B(C_6H_5)_4$	62.20	4.10	12.15	10.85	61.93	4.27	12.73	10.49
$Ni_2(C_8H_6N_2)_4(NCS)_2B(C_6H_5)_4$	64.89	4.13	13.05	10.93	64.70	4.55	12.45	10.81
$Ni_2(C_8H_6N_2)_4Cl_2PF_6$	45.00	2.83	13.12	13.76	45.11	2.86	13.41	13.40
$Ni_2(C_8H_6N_2)_4Br_2PF_6$	40.73	2.59	11.87	12.45	40.55	2.64	11.89	12.10
$Ni_2(C_8H_6N_2)_4I_2PF_6$	37.07	2.33	10.80	11.32	36.91	2.20	10.89	11.36
$Ni_2(C_9H_8N_2)_4Cl_2B(C_6H_5)_4$	66.46	4.83	10.33	10.83	65.81	5.12	9.90	10.70
$Ni_2(C_9H_8N_2)_4Br_2B(C_6H_5)_4$	61.42	4.46	9.55	10.00	61.71	4.94	9.01	9.60
$Ni_2(C_9H_8N_2)_4I_2B(C_6H_5)_4$	56.86	4.13	8.84	9.26	56.03	4.11	8.50	8.90
$Ni_2(C_9H_8N_2)_4(NCS)_2B(C_6H_5)_4$	65.92	4.64	12.40	10.39	65.05	4.70	12.14	10.46
$Ni_2(C_9H_8N_2)_4Cl_2PF_6$	47.54	3.55	12.32	12.91	47.10	3.90	12.02	12.11
$Ni_2(C_9H_8N_2)_4Br_2PF_6$	43.42	3.28	11.25	11.76	42.75	3.28	11.14	11.40
$Ni_2(C_9H_8N_2)_4I_2PF_6$	39.60	3.10	10.26	10.73	39.77	3.10	10.16	10.45

[a] napy is 1,8-naphthyridine ($C_8H_6N_2$). [b] menapy is 4-methyl-1,8-naphthyridine ($C_9H_8N_2$).

mulas $Ni(napy)_2X_2$ and $Ni(napy)_2XB(C_6H_5)_4$ (X = halogen). A particularly interesting series of dimeric complexes of the general formula $[Ni_2(napy)_4X_2]Y$ (X = halogen, NCS, NO_3; Y = PF_6, $B(C_6H_5)_4$) has been isolated in which the nickel has the formal oxidation state of +1.5. The electronic and nmr spectra and the magnetic measurements have been used to characterize the complexes.

A complete X-ray structural analysis has been carried out for the compound $[Ni_2(napy)_4Br_2]B(C_6H_5)_4$.

A preliminary account of part of this research has already been published.[2]

Experimental Section

Materials. All the reagents were reagent grade; the solvents were dried according to the usual procedures. 1,8-Naphthyridine (napy) and 4-methyl-1,8-naphthyridine (menapy) were prepared according to the procedure described by Paudler and Kress.[3] All the metal complexes were filtered onto a glass funnel, washed with an ethanol-petroleum ether mixture, and dried *in vacuo* at 60°. The analytical data for the complexes are reported in Table I.

Preparations. $Ni(napy)_2X_2$ (X = Br, I). To a hot solution of the appropriate nickel(II) halide (1 mmol) in butan-1-ol (25 ml) a hot solution of the ligand in the same solvent (25 ml) was added. On reducing the volume brown crystals were obtained.

$Ni(napy)_2XB(C_6H_5)_4$ (X = Cl, Br). To a hot solution of the appropriate nickel(II) halide (1 mmol) in ethanol (20 ml) a hot solution of the ligand (2 mmol) and a hot solution of sodium tetraphenylborate (1 mmol) in the same solvent (20 ml) were added. A pale green precipitate was obtained which could not be recrystallized due to its insolubility in all the common organic solvents.

$Ni_2L_4X_2B(C_6H_5)_4$ (L = napy, 4-menapy) (X = Cl, Br, I, SCN, NO_3). To a boiling solution of the appropriate nickel(II) salt NiX_2 (1 mmol) in butan-1-ol (20 ml) boiling solutions of the ligand (2 mmol) and sodium tetraphenylborate (1 mmol) in butan-1-ol (20 ml) were added in rapid succession. At first the solution became turbid, and in the case of the chloro and bromo salts a pale green solid was separated. On further boiling, the solution turned black-green and black crystals were precipitated.

These were separated from the pale green crystals previously formed by dissolving in acetone. By evaporation of this acetone solution to small volume and addition of ethanol in small portions black crystals were precipitated.

$Ni_2L_4X_2PF_6$ (L = napy, 4-menapy) (X = Cl, Br, I). Hot ethanol solutions of the appropriate nickel(II) halide (1 mmol), of the ligand (2 mmol), and of tetrabutylammonium hexafluorophosphate (1 mmol) were mixed under nitrogen atmosphere, the resulting volume being 50 ml. To the clear solution a solution of sodium tetrahydroborate (0.5 mmol) in ethanol (10 ml) was added in small portions. The solution turned black-green and black crystals precipitated.

Instrumentation. Solution and diffuse reflectance spectra, ^1H nuclear magnetic resonance spectra and variable-temperature magnetic susceptibilities have been recorded as described elsewhere.[4]

Collection and Reduction of X-Ray Data. Single-crystal data were measured using a Philips computer-controlled PW 1100 single-crystal diffractometer.

The specimen was mounted on the diffractometer in an arbitrary orientation, but account was taken that the X-ray path inside the crystal was as short as possible at $\chi = 0°$. The space group was determined as the monoclinic $P2_1/c$, the lattice constants being (Mo $K\alpha$ = 0.7107, monochromatized with a flat graphite monochromator crystal) a = 9.931 Å, b = 32.311 Å, c = 16.535 Å, and β = 101.5°.

All reflections were split into two separate peaks largely differing in intensities; only the most intense peaks were considered suitable for data collection. The splitting was probably due to the poor quality of the crystals. The specimen however was the best we could obtain by synthesis.

A density of 1.43 g cm^{-3} is calculated on the basis of four formula units of $[Ni_2(napy)_4Br_2]B(C_6H_5)_4$ per cell, in satisfactory agreement with the experimental density of 1.41 g cm^{-3} observed by flotation.

The crystal used for data collection can be described approximately as a lath with dimensions of 0.05 × 0.3 × 0.7 mm which respectively correspond to the b, a, and c direct axes of the cell.

Data were collected by a ϑ–2ϑ scan technique with a scan width of 1.0° employed for all reflections. The scanning time for reflections was 14 sec and background counts of 7 sec were taken at the end of each scan.

Three standard reflections monitored at regular intervals throughout the period of data collection showed no variations in intensity beyond those expected for counting statistics. The intensities of a total 5011 independent reflections with $\vartheta < 20°$ were measured.

Lorentz and polarization effects were considered in data reduction, but no absorption correction was made (linear absorption coefficient 24.0 cm^{-1}). In estimation of the standard deviations of the individual intensities a value of 0.02 was used for the p factor

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Table II. Positional Parameters ($\times 10^4$) and Thermal Parameters[a] ($\times 10^2$)

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Br(1)	1609 (2)	3417 (1)	891 (2)	306 (18)	570 (22)	434 (20)	13 (14)	133 (12)	37 (15)
Br(2)	−4148 (2)	3371 (1)	3388 (1)	343 (18)	552 (22)	329 (19)	41 (14)	118 (11)	66 (14)
Ni(1)	−321 (3)	3404 (1)	1780 (2)	235 (20)	301 (22)	248 (20)	−3 (15)	37 (13)	17 (16)
Ni(2)	−2132 (3)	3395 (1)	2562 (2)	243 (20)	281 (21)	229 (20)	7 (15)	8 (13)	−4 (15)
N(1)	−1221 (15)	2876 (5)	1157 (9)	25 (85)	409 (113)	180 (92)	87 (75)	−17 (68)	−10 (76)
N(2)	−3308 (17)	3082 (5)	1532 (9)	317 (106)	371 (109)	122 (92)	−24 (82)	−136 (80)	13 (78)
N(3)	767 (16)	3003 (5)	2698 (10)	195 (92)	255 (105)	279 (105)	−111 (75)	89 (80)	−51 (85)
N(4)	−1293 (18)	2802 (5)	2994 (9)	339 (106)	217 (101)	101 (89)	65 (82)	−61 (77)	−4 (74)
N(5)	464 (18)	3900 (5)	2524 (11)	345 (105)	367 (117)	334 (118)	−132 (85)	94 (88)	80 (92)
N(6)	−752 (17)	3711 (5)	3492 (10)	318 (105)	268 (107)	169 (101)	−13 (83)	−57 (81)	−18 (81)
N(7)	−1667 (18)	3769 (6)	956 (10)	408 (112)	411 (120)	60 (96)	−66 (89)	7 (80)	79 (80)
N(8)	−2757 (17)	3969 (5)	2008 (10)	288 (97)	366 (112)	185 (102)	21 (86)	−50 (78)	14 (85)

[a] The form of the anisotropic thermal parameters is given by $\exp[-(\Sigma_i \Sigma_j h_i h_j r_i^* r_j^* B_{ij})]/4$ with $i, j = 1, 2, 3$ where r_i^* is the ith reciprocal axis.

which determines the minimum value of $\sigma(I)/I$ in the absence of any contribution from counting statistics. A total of 2402 reflections were observed at a 3σ limit and these were used throughout the structure determination and subsequent refinement.

Solution and Refinement of the Structure. The solution of the structure was initially approached using a Patterson map and heavy-atom techniques. A trial with direct methods gave confirmation of the correct interpretation of the Patterson synthesis.

Three Fourier syntheses following the initial E map gave the coordinates of all the 69 nonhydrogen atoms, the R factor ($R = 100(\Sigma ||F_o| - |F_c|| / \Sigma |F_o|)$ at the end of this Fourier approach being 18. Least-squares refinement of the positional and thermal isotropic parameters of these atoms converged to a discrepancy factor 10.1. Two further least-squares cycles with anisotropic thermal parameters assigned to the polyhedron's 12 atoms reduced the R factor (defined above) to 7.7 and the weighted R factor ($R_w = 100\ [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w |F_o|^2]^{1/2}$ was 8.5. The weights used were taken as $1/\sigma(F_o)$. The effects of anomalous dispersion $\Delta f'$ and $\Delta f''$ for Br and Ni were also included in calculations of F_c.

Benzene hydrogen atoms were placed in calculated positions and assigned arbitrary thermal parameters of 4.0 Å^2. Positional and thermal parameters for the hydrogen atoms were not varied in any least-squares cycle but were recalculated before each subsequent refinement cycle. Prior to the incorporation of the hydrogen atoms in the refinement a difference map was examined and showed electron density at the calculated positions.

The final conventional R factor is 7.2 and the weighted factor is 8.5. Lists of atomic positional and thermal parameters together with estimated standard deviations are given in Tables II and III. The list of observed and calculated structure factors is also available.

Single-Crystal Polarized Electronic Spectra. Thin plates of the $[Ni_2(napy)_4Br_2]B(C_6H_5)_4$ complex were used to record single-crystal polarized electronic spectra. The well-developed faces were parallel to the (010) plane. The spectra were recorded with the apparatus previously described[5] along the extinction directions (r, s) on the (010) face. r is about 20° from $+c$ toward $+a$, and c is orthogonal to it. No spectra were recorded on different faces due to the thinness of the crystal and to the high absorption coefficients of the bands.

Results and Discussion

Reaction of nickel(II) bromide or iodide with napy in butan-1-ol solutions produced brown powders which, on the basis of the analytical data, can be formulated as $Ni(napy)_2X_2$. The complexes are insoluble in all the common organic solvents. The spectral and magnetic data are reported in Table IV. Figure 1 reports the electronic spectrum of the bromide derivative. These data, in the absence of a full characterization in solution, do not allow a safe assignment of the stereochemistry of the complexes which may range from pentacoordinated to distorted octahedral.

When alcoholic solutions of nickel(II) salts, of the ligand and of sodium tetraphenylborate are mixed, different products are obtained depending on the nature of the nickel salts, of the solvent, and of temperature. If the solvent is ethanol

Table III. Positional Parameters ($\times 10^4$) and Thermal Parameters ($\times 10^2$)

Atom	x	y	z	B, Å^2
C(1)	−578 (21)	2611 (7)	807 (14)	258 (53)
C(2)	−1174 (22)	2283 (7)	356 (13)	341 (57)
C(3)	−2564 (23)	2194 (7)	268 (14)	320 (58)
C(4)	−3322 (21)	2468 (7)	621 (13)	281 (55)
C(5)	−4785 (22)	2451 (7)	585 (14)	362 (57)
C(6)	−5431 (23)	2744 (7)	967 (14)	406 (60)
C(7)	−4673 (25)	3058 (7)	1446 (14)	336 (59)
C(8)	−2553 (22)	2814 (6)	1117 (13)	225 (49)
C(9)	2126 (22)	2962 (7)	2770 (13)	278 (54)
C(10)	2783 (24)	2608 (8)	3162 (15)	464 (64)
C(11)	2052 (24)	2304 (7)	3444 (14)	394 (61)
C(12)	650 (22)	2344 (7)	3387 (13)	293 (54)
C(13)	−225 (22)	2050 (7)	3641 (13)	347 (54)
C(14)	−1579 (22)	2136 (7)	3587 (14)	367 (57)
C(15)	−2099 (21)	2514 (7)	3234 (13)	250 (54)
C(16)	85 (23)	2722 (7)	3020 (13)	247 (52)
C(17)	1383 (25)	4143 (8)	2312 (15)	465 (63)
C(18)	2217 (28)	4453 (9)	2853 (18)	726 (78)
C(19)	1996 (27)	4474 (9)	3611 (17)	594 (72)
C(20)	1068 (23)	4221 (8)	3902 (15)	417 (60)
C(21)	781 (24)	4221 (8)	4693 (15)	450 (62)
C(22)	−147 (24)	3975 (8)	4897 (15)	423 (62)
C(23)	−939 (22)	3726 (7)	4269 (16)	339 (58)
C(24)	262 (24)	3942 (7)	3295 (16)	288 (54)
C(25)	−1607 (23)	3793 (7)	177 (16)	399 (61)
C(26)	−2307 (22)	4100 (8)	−372 (14)	366 (59)
C(27)	−3079 (23)	4369 (8)	−93 (15)	434 (61)
C(28)	−3215 (22)	4354 (7)	735 (14)	348 (57)
C(29)	−4034 (24)	4628 (7)	1089 (15)	458 (62)
C(30)	−4116 (23)	4564 (7)	1899 (15)	405 (61)
C(31)	−3522 (22)	4229 (7)	2332 (14)	290 (55)
C(32)	−2567 (22)	4035 (7)	1219 (15)	272 (55)
C(33)	3938 (21)	1280 (7)	1322 (13)	333 (51)
C(34)	2961 (22)	1576 (8)	1518 (13)	399 (55)
C(35)	2178 (24)	1844 (8)	925 (16)	543 (63)
C(36)	2338 (22)	1809 (7)	96 (14)	448 (58)
C(37)	3265 (20)	1548 (7)	−136 (12)	342 (49)
C(38)	4058 (22)	1285 (7)	467 (14)	384 (56)
C(39)	4088 (21)	509 (7)	1653 (13)	326 (51)
C(40)	4806 (23)	220 (8)	1236 (14)	467 (60)
C(41)	4092 (26)	−136 (8)	883 (15)	577 (66)
C(42)	2742 (28)	−208 (8)	924 (16)	577 (69)
C(43)	2059 (25)	45 (8)	1304 (15)	499 (63)
C(44)	2719 (25)	421 (8)	1680 (15)	480 (63)
C(45)	4579 (21)	1085 (7)	2944 (13)	300 (53)
C(46)	5083 (23)	1459 (7)	3258 (15)	438 (60)
C(47)	4950 (24)	1587 (8)	4034 (16)	481 (62)
C(48)	4265 (25)	1342 (9)	4465 (15)	580 (69)
C(49)	3769 (26)	959 (9)	4192 (17)	663 (73)
C(50)	3947 (25)	826 (8)	3388 (17)	546 (68)
C(51)	6391 (21)	976 (7)	2010 (13)	338 (52)
C(52)	7276 (24)	657 (7)	2371 (14)	446 (58)
C(53)	8733 (26)	692 (8)	2457 (15)	524 (68)
C(54)	9314 (25)	1032 (9)	2220 (16)	589 (69)
C(55)	8534 (28)	1367 (8)	1849 (16)	614 (73)
C(56)	7068 (25)	1313 (7)	1754 (14)	465 (61)
B(1)	4783 (26)	941 (8)	1995 (16)	337 (63)

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Table IV. Physical Properties of napy and menapy Complexes of Nickel

Compd	Magnetic moment,[a] BM	Λ_M, cm^2 ohm^{-1} mol^{-1}		Electronic spectra[d]
		b	*c*	
$Ni(napy)_2Br_2$	3.18			7.0, 12.1, 18.5 sh, 22.0
$Ni(napy)_2I_2$	3.25			6.9, 12.3
$Ni(menapy)_2Br_2$	3.29			7.6, 12.8, 22.2
$Ni(menapy)_2(NCS)_2$	3.18			8.9, 15.1, 25
$Ni(napy)_2ClB(C_6H_5)_4$	3.36			8.6, 15.2
$Ni(napy)_2BrB(C_6H_5)_4$	3.34			8.6, 14.8
$[Ni(napy)_4Cl_2]B(C_6H_5)_4$	4.23	50	23	9.9 (105), 16.6 (3007), 24.1 (4009), 25.3 (4060) 9.9, 17.4
$[Ni(napy)_4Br_2]B(C_6H_5)_4$	4.19	54	26	9.7 (110), 16.4 (3385), 24.7 sh, 25.8 (3977) 9.6, 16.6
$[Ni(napy)_4I_2]B(C_6H_5)_4$	4.34	57	25	9.3 (107), 15.6 (4590), 22.2 sh 9.2, 16.1
$[Ni(napy)_4(NO_3)_2]B(C_6H_5)_4$	4.21	55	22	9.8 (95), 17.5 (2608), 26.7 (4173) 10.1, 17.5
$[Ni(napy)_4(NCS)_2]B(C_6H_5)_4$	4.20	53	26	10.7 (120), 17.2 (3645), 25 sh; 26.0 (4363) 10.7, 17.4, 26.6
$[Ni_2(napy)_4Cl_2]PF_6$	4.21	76	44	9.8 (106), 16.6 (2620), 25.0 (3300) 9.8, 17.2, 26.3
$[Ni_2(napy)_4Br_2]PF_6$	4.12	89	31	9.5 (88), 16.5 (3090), 25.9 (4100) 9.7, 16.5, 26.6
$[Ni_2(napy)_4I_2]PF_6$	4.23	81	30	9.3 (117), 15.6 (3000), 22.2 sh 9.5, 16.6, 26.6
$[Ni_2(menapy)_4Cl_2]B(C_6H_5)_4$	4.40	50	26	9.9 (83), 16.6 (3140), 24.3 sh, 25.0 (3640) 10.0, 17.5, 26.6
$[Ni_2(menapy)_4Br_2]B(C_6H_5)_4$	4.21	27	51	9.7 (88), 16.5 (2849), 25.6 (4037) 9.6, 16.7
$[Ni_2(menapy)_4I_2]B(C_6H_5)_4$	4.24	26	59	9.3 (117), 15.6 (3000), 22.2 sh 9.3, 16.5
$[Ni_2(menapy)_4(NCS)_2]B(C_6H_5)_4$	4.26	26	52	10.7 (140), 17.2 (4115), 25.6 (5055) 10.8, 16.7
$[Ni_2(menapy)_4Cl_2]PF_6$	4.20	35	80	9.8 (100), 16.9 (3000), 25.0 (4200) 9.9, 17.0
$[Ni_2(menapy)_4Br_2]PF_6$	4.23	35	88	9.5 (109), 16.6 (3400), 25.6 (4700) 9.5, 16.6, 26.6
$[Ni_2(menapy)_4I_2]PF_6$	4.13	76	32	9.3 (102), 15.8 (3970), 22.2 sh 9.4, 16.6

[a] Measured at 293 K. [b] Nitroethane solution. [c] 1,2-Dichloroethane solution. [d] The solution spectra with ϵ in parentheses are reported in the first line and the reflectance spectra are reported on the second line for each complex.

and X = Cl or Br, pale green precipitates are obtained which, on the basis of the analytical data, are formulated as $Ni(napy)_2XB(C_6H_5)_4$. These complexes are insoluble in all the common organic solvents. The spectral and magnetic data are reported in Table IV; Figure 1 reports the spectrum of the bromide derivative. The values of the magnetic moments (3.34 and 3.36 BM) at 20° and the positions of the maxima in the electronic spectra (8.6 and 15 kK) are in good agreement with the values expected for octahedral nickel(II) complexes.[6] The third transition expected for octahedral nickel(II) is masked by a strong charge-transfer band. On this basis a polymeric octahedral structure, presumably with halogen bridges, is proposed.

If butan-1-ol is used as a solvent, the solution becomes black-green on boiling and black crystals precipitate which can be separated from the green precipitate previously formed by dissolution in acetone. The analytical data are in agreement with the formula $Ni_2(napy)_4X_2B(C_6H_5)_4$. The same formulation is valid for the corresponding menapy complexes.

The formal oxidation number of the nickel ion is +1.5, indicating that a reduction has taken place. The reduction is associated with the presence of sodium tetraphenylborate. If sodium hexafluorophosphate is used in place of sodium tetraphenylborate, the black precipitate is obtained only by addition of sodium tetrahydroborate. The analytical data are in agreement with the general formula $Ni_2(napy)_4X_2PF_6$.

A complete X-ray analysis has been made for the complex $Ni_2(napy)_4Br_2B(C_6H_5)_4$. The structure consists of binuclear complex cations $[Ni_2(napy)_4Br_2]^+$ and $B(C_6H_5)_4^-$ anions as shown in Figure 2. The stereochemistry of the dimeric unit is shown in Figure 3. Each nickel atom is square pyramidal with four nitrogen atoms (of four different ligand molecules) forming the base and one bromine atom the apex. These two equivalent moieties are held together by the four bridging napy molecules, the two nickel atoms being only 2.415 (4) Å apart. The geometry of the coordination polyhedron is on the whole a bicapped tetragonal antiprism, the average twist angle between the two tetragonal pyramids being 25.1°.

Intramolecular distances and angles within the coordination polyhedron of the nickel atoms and in the $B(C_6H_5)_4^-$ anion are given in Table V. The nickel-nickel distance of 2.415 (4) Å compares well with those found in other dimeric nickel complexes for which metal-metal interaction has been sug-

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(6) L. Sacconi, *Transition Metal Chem.*, 4, 199 (1968).

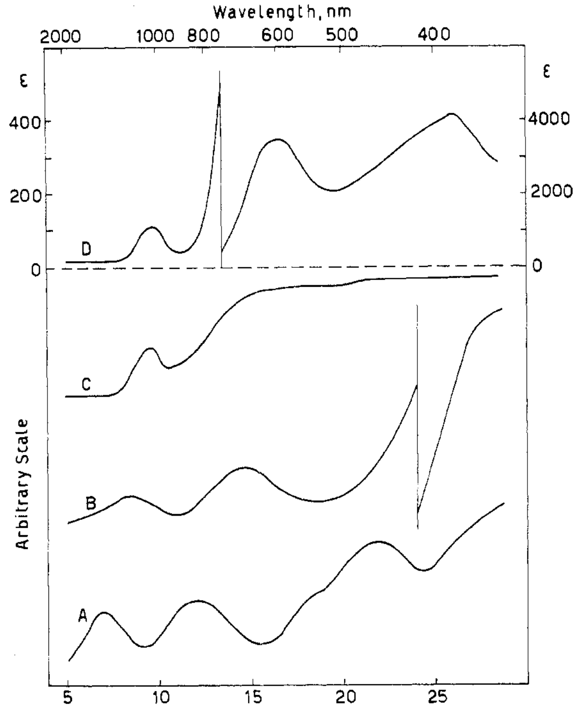

Figure 1. Electronic spectra: (A) Ni(napy)$_2$Br$_2$, solid; (B) Ni(napy)$_2$Br$_2$B(C$_6$H$_5$)$_4$, solid; (C) [Ni$_2$(napy)$_4$Br$_2$]B(C$_6$H$_5$)$_4$, solid; (D) Ni$_2$(napy)$_4$Br$_2$B(C$_6$H$_5$)$_4$, 1,2-dichloroethane solution.

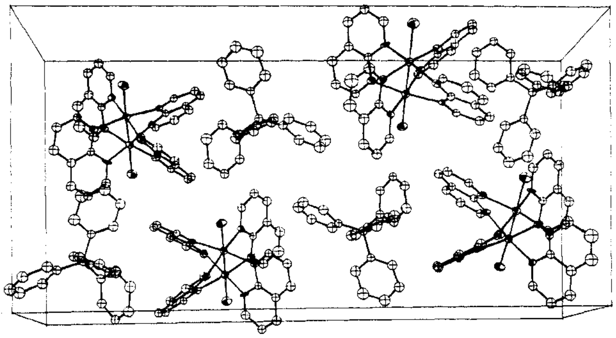

Figure 2. Contents of the unit cell as viewed down the *a* axis.

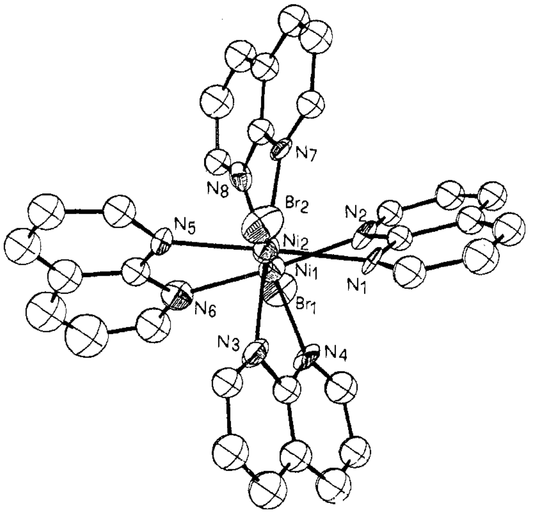

Figure 3. Perspective view of the dimeric cation of [Ni$_2$(napy)$_4$Br$_2$]B(C$_6$H$_5$)$_4$.

Table V. Intramolecular Distances (Å) and Angles (deg) in the Coordination Polyhedron and Anion B(C$_6$H$_5$)$_4^-$

Distances

Ni(1)-Ni(2)	2.415 (4)	B(1)-C(33)	1.664 (34)
Ni(1)-Br(1)	2.640 (4)	B(1)-C(39)	1.605 (34)
Ni(2)-Br(2)	2.641 (4)	B(1)-C(45)	1.688 (35)
Ni(1)-N(1)	2.094 (17)	B(1)-C(51)	1.596 (33)
Ni(1)-N(3)	2.120 (16)		
Ni(1)-N(5)	2.073 (18)	C-C (av for ring 1)	1.416 (33)
Ni(1)-N(7)	2.075 (17)	C-C (av for ring 2)	1.396 (35)
Ni(2)-N(2)	2.118 (16)	C-C (av for ring 3)	1.374 (36)
Ni(2)-N(4)	2.148 (17)	C-C (av for ring 4)	1.399 (35)
Ni(2)-N(6)	2:107 (17)		
Ni(2)-N(8)	2.102 (18)		

Angles

Br(1)-Ni(1)-Ni(2)	178.5 (2)	N(6)-Ni(2)-N(8)	89.2 (6)
Br(2)-Ni(2)-Ni(1)	178.5 (2)	Ni(2)-Ni(1)-N(1)	87.9 (4)
Br(1)-Ni(1)-N(1)	91.4 (4)	Ni(2)-Ni(1)-N(3)	86.3 (4)
Br(1)-Ni(1)-N(3)	94.9 (4)	Ni(2)-Ni(1)-N(5)	85.6 (5)
Br(1)-Ni(1)-N(5)	95.1 (5)	Ni(2)-Ni(1)-N(7)	84.7 (5)
Br(1)-Ni(1)-N(7)	93.9 (5)	Ni(1)-Ni(2)-N(2)	85.7 (4)
Br(2)-Ni(2)-N(2)	92.8 (4)	Ni(1)-Ni(2)-N(4)	84.7 (4)
Br(2)-Ni(2)-N(4)	94.9 (4)	Ni(1)-Ni(2)-N(6)	86.6 (5)
Br(2)-Ni(2)-N(6)	94.9 (5)	Ni(1)-Ni(2)-N(8)	86.7 (5)
Br(2)-Ni(2)-N(8)	93.6 (5)		
N(1)-Ni(1)-N(3)	88.0 (6)	C(33)-B(1)-C(39)	102.1 (1.8)
N(1)-Ni(1)-N(5)	172.6 (7)	C(33)-B(1)-C(45)	107.7 (1.8)
N(1)-Ni(1)-N(7)	88.9 (6)	C(33)-B(1)-C(51)	109.4 (1.8)
N(3)-Ni(1)-N(5)	88.1 (7)	C(39)-B(1)-C(45)	116.3 (1.9)
N(3)-Ni(1)-N(7)	170.7 (6)	C(39)-B(1)-C(51)	115.2 (1.9)
N(5)-Ni(1)-N(7)	94.0 (7)	C(45)-B(1)-C(51)	105.8 (1.8)
N(2)-Ni(2)-N(4)	87.7 (6)		
N(2)-Ni(2)-N(6)	172.3 (6)	C-C-C (av for ring 1)	120.0 (2.0)
N(2)-Ni(2)-N(8)	90.0 (6)	C-C-C (av for ring 2)	120.0 (2.2)
N(4)-Ni(2)-N(6)	91.9 (6)	C-C-C (av for ring 3)	120.0 (2.3)
N(4)-Ni(2)-N(8)	171.3 (6)	C-C-C (av for ring 4)	120.0 (2.2)

gested to be operative.[7,8] The two nickel atoms which have identical coordination spheres lie 0.146 (3) Å above the planes defined by the nitrogen atoms, the average Br-Ni-N angle being 94°. The displacement of the nickel atom is small compared with that generally found in high-spin nickel(II) square-pyramidal complexes,[9] and may be due to the interaction with the other nickel atom to complete an octahedral stereochemistry. The mean nickel-nickel distance is 2.105 (17) Å and the nickel-bromine distance is 2.614 (4) Å. These values appear to be a little larger than the values generally found in octahedral nickel-pyridine complexes,[10] as would be expected due to the reduced charge on the metal ions.

The intramolecular distances and angles within the ligand are reported in Table VI. On the average the symmetric bond distances and angles on the napy molecule are equal within the standard deviations. The napy ligands are not strictly planar. In particular the two nitrogen atoms are displaced from the mean plane in opposite directions by about 0.07 Å (Table VII). A similar distortion, although less pronounced, was observed in the structure of the free ligand[11] and was mostly attributed to the repulsion between the nonbonded pairs localized on the nitrogen atoms. However in the complex [Fe(napy)$_4$](ClO$_4$)$_2$ the napy molecules were found to be strictly planar.[12] The distortion observed in the present case makes it scarcely probable that the main distorting force is the repulsion of the lone pairs on the nitrogen atoms.

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Table VI. Bond Lengths (Å) and Angles (deg) in the Ligand Molecule[a]

	Distances		
N(1)-C(1)	1.304 (29)	C(5)-C(6)	1.352 (33)
C(1)-C(2)	1.418 (35)	C(6)-C(7)	1.398 (33)
C(2)-C(3)	1.341 (41)	N(2)-C(7)	1.331 (31)
C(3)-C(4)	1.384 (33)	N(1)-C(8)	1.334 (28)
C(4)-C(5)	1.412 (32)	N(2)-C(8)	1.378 (29)
C(4)-C(8)	1.441 (32)		
	Angles		
N(1)-C(8)-N(2)	117.0 (1.9)	C(3)-C(4)-C(8)	116.2 (2.0)
C(1)-N(1)-C(8)	117.3 (1.9)	C(5)-C(4)-C(8)	117.8 (2.0)
C(7)-N(2)-C(8)	120.1 (1.8)	C(4)-C(5)-C(6)	120.7 (2.1)
N(1)-C(1)-C(2)	123.3 (2.1)	C(5)-C(6)-C(7)	119.9 (2.1)
C(1)-C(2)-C(3)	119.3 (2.2)	C(6)-C(7)-N(2)	122.0 (2.1)
C(2)-C(3)-C(4)	120.1 (2.3)	N(1)-C(8)-C(4)	123.3 (2.0)
C(3)-C(4)-C(5)	126.0 (2.2)	N(2)-C(8)-C(4)	119.6 (2.0)

[a] The values are averaged between the four napy molecules present in the complex cation, individual differences from the average being all within 3σ. The σ's are the averaged standard deviations from refinement. The labeling of the atoms is relative only to those of the first molecule.

Table VII. Displacements (Å) of the napy Atoms from the Mean Plane

First Ligand Molecule		Second Ligand Molecule	
N(1)	−0.048	N(3)	−0.071
C(1)	−0.020	C(9)	−0.022
C(2)	−0.004	C(10)	0.049
C(3)	0.046	C(11)	0.027
C(4)	0.004	C(12)	−0.002
C(5)	−0.010	C(13)	−0.051
C(6)	−0.049	C(14)	−0.010
C(7)	−0.001	C(15)	0.011
C(8)	0.016	C(16)	−0.002
N(2)	0.066	N(4)	0.070
Third Ligand Molecule		**Fourth Ligand Molecule**	
N(5)	0.051	N(7)	0.098
C(17)	0.026	C(25)	0.003
C(18)	−0.032	C(26)	−0.054
C(19)	−0.043	C(27)	−0.041
C(20)	0.019	C(28)	0.030
C(21)	0.019	C(29)	0.036
C(22)	0.045	C(30)	0.047
C(23)	−0.032	C(31)	−0.058
C(24)	0.007	C(32)	0.010
N(6)	−0.061	N(8)	−0.070
Average among the Four napy Molecules			
$N(1)_{av}$	−0.062	$C(5)_{av}$	−0.036
$C(1)_{av}$	−0.033	$C(6)_{av}$	−0.036
$C(2)_{av}$	0.034	$C(7)_{av}$	0.010
$C(3)_{av}$	0.032	$C(8)_{av}$	0.007
$C(4)_{av}$	0.013	$N(2)_{av}$	0.071

The values of the effective magnetic moments of the $[Ni_2(napy)_4X_2]Y$ complexes (calculated for the dimeric units) are in the range 4.19–4.33 BM (see Table IV) in agreement with the presence of three unpaired electrons. Variable-temperature measurements, down to 85 K, of the magnetic susceptibility of the $[Ni_2(napy)_4Br_2]B(C_6H_5)_4$ complex did not show any significant departure from Curie–Weiss behavior (the Weiss constant Θ was found to be −3 K) suggesting that if any coupling of the two nickel atoms is present it must be small. In the previous communication[2] a rationale was offered to explain the presence of three unpaired electrons using the basis of a weakly coupled chromophore model.[13,14]

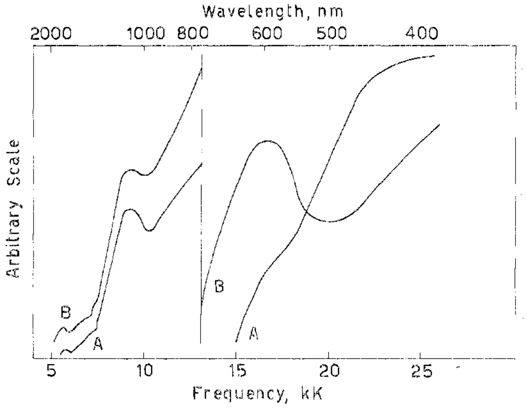

Figure 4. Single-crystal polarized electronic spectra of the $Ni_2(napy)_4Br_2B(C_6H_5)_4$ complex: (A) spectrum recorded along *r*; (B) spectrum recorded along *s*.

That the structures of the complexes appear to be retained in solution is shown by the close correspondence of the solution and solid-state electronic spectra (Table IV and Figure 1) and by the values of the conductivities of all the complexes of the series which agree with the presence of 1:1 electrolytes (Table IV).

The ^1H nuclear magnetic resonance spectra of the $[Ni_2(napy)_4Br_2]B(C_6H_5)_4$ complex in CD_3NO_2 solutions show only two peaks which can be attributed to the napy protons. The signals are broad (half-width 1 ppm) and both downfield from internal TMS. A signal at −35.2 ppm can be attributed to the 3,6 H and another at −40.1 ppm to the 4,5 H on the basis of bandwidth and by comparison with the spectra of the 4-menapy derivative. In the latter spectra the methyl signal appears upfield at +12.1 ppm. The signal of the 2,7 H is presumably so large that it cannot be detected. The isotropic shift pattern in this complex is far different from that which was observed in nickel(II) complexes with napy and with other pyridine-type ligands.[15] This difference must be attributed mainly to a sizable π contribution to the spin density delocalization. A pseudocontact contribution too may be operative in these dimeric units but it does not seem probable that it is the most important effect, since in this case it would be expected to shift also the 4-methyl signal downfield, which on the contrary is observed upfield as frequently observed in π spin density delocalization mechanisms.[16]

The electronic spectra of the dimeric complexes show three bands in the range 4–26 kK (Table IV and Figure 1). The single-crystal polarized electronic spectra of the complex $[Ni_2(napy)_4Br_2]B(C_6H_5)_4$ are reported in Figure 4. The spectrum recorded along *r* is 0.80 parallel and 0.20 perpendicular and the spectrum along *s* is 0.20 parallel and 0.80 perpendicular if the Ni–Br axis is assumed as the *z* axis of the complex. The highest energy band is in some cases split into two. The lowest frequency band is far less intense than the others ($\epsilon \sim 10^2$ *vs.* $\sim 10^3$ for the other two bands) and it can be assigned to d–d transitions. The order and the magnitude of the shifts of the maxima on changing the axial ligand are in qualitative agreement with the position of the ligand in the spectrochemical series.[17] In the single-crystal electronic spectrum no clear polarization properties were observed for this band.

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(14) In Figure 2 of ref 2 the B_1 and B_2 labels should be interchanged.

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The two high-frequency bands may presumably be assigned to charge-transfer transitions. The 16-kK band is presumably due to an inverted electron-transfer transition[17] (*i.e.*, from the metal to the ligand). The ligand in fact has low-lying π^* levels, as shown by the electronic spectrum, where the band in the region 33-39 kK has been attributed to π-π^* transitions.[18] Such bands have been observed also in the present case, practically unshifted compared to the free ligand. It is possible then that napy acts similarly to other nitrogen heterocyclic ligands, such as phenanthroline and dipyridine, which are known to stabilize the low oxidation states of transition metal ions.[19] The single-crystal spectrum shows that the band at 16 kK is polarized perpendicularly, as would be expected for a charge-transfer transition involving the nickel and nitrogen atoms.[20] The 26-kK band could not be satisfactorily analyzed since it is at the limit of operation of our apparatus.

Acknowledgment. Thanks are due to Mr. G. Scapacci for technical assistance.

Registry No. Ni(napy)$_2$Br$_2$, 51425-51-5; Ni(napy)$_2$I$_2$, 51425-52-6; Ni(menapy)$_2$Br$_2$, 51464-62-1; Ni(menapy)$_2$(NCS)$_2$, 51425-21-9; Ni(napy)$_2$ClB(C$_6$H$_5$)$_4$, 51425-23-1; Ni(napy)$_2$BrB(C$_6$H$_5$)$_4$, 51425-25-3; [Ni$_2$(napy)$_4$Cl$_2$]B(C$_6$H$_5$)$_4$, 51518-88-8; [Ni$_2$(napy)$_4$Br$_2$]B(C$_6$H$_5$)$_4$, 39391-56-5; [Ni$_2$(napy)$_4$I$_2$]B(C$_6$H$_5$)$_4$, 51518-89-9; [Ni$_2$(napy)$_4$(NO$_3$)$_2$]B(C$_6$H$_5$)$_4$, 51518-90-2; [Ni$_2$(napy)$_4$(NCS)$_2$]B(C$_6$H$_5$)$_4$, 51518-91-3; [Ni$_2$(napy)$_4$Cl$_2$]PF$_6$, 51518-92-4; [Ni$_2$(napy)$_4$Br$_2$]PF$_6$, 51518-93-5; [Ni$_2$(napy)$_4$I$_2$]PF$_6$, 51518-94-6; [Ni$_2$menapy)$_4$Cl$_2$]B(C$_6$H$_5$)$_4$, 51518-95-7; [Ni$_2$(menapy)$_4$Br$_2$]B(C$_6$H$_5$)$_4$, 51518-96-8; [Ni$_2$(menapy)$_4$I$_2$]B(C$_6$H$_5$)$_4$, 51518-97-9; [Ni$_2$(menapy)$_4$(NCS)$_2$]B(C$_6$H$_5$)$_4$, 51518-98-0; [Ni$_2$(menapy)$_4$Cl$_2$]PF$_6$, 51518-99-1; [Ni$_2$(menapy)$_4$Br$_2$]PF$_6$, 51519-00-7; [Ni$_2$(menapy)$_4$I$_2$]PF$_6$, 51519-01-8.

Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W. Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number INORG-74-1985.

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Kinetics of the Reversible Replacement of Amine by Chloride under the Trans Effect of Dimethyl Sulfoxide in Square-Planar Platinum(II) Complexes

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The rate constants for the forward and reverse steps of the reaction $[PtCl_3(DMSO)]^- + am \rightleftarrows$ *trans*-$[PtCl_2(DMSO)(am)] + Cl^-$ (DMSO = S-bonded dimethyl sulfoxide; am is one of a number of amines covering a wide range of basicity) have been determined in methanol at 30.0° at constant ionic strength (0.50). The forward reaction goes mainly by way of the direct bimolecular attack of amine on the complex and the rate constant does not depend greatly upon the nature of the nucleophile, although small trends can be detected within the subgroups of amine used. The reverse reaction obeys the usual two-term rate law observed in square-planar substitution, and the nucleophile-independent, solvolytically controlled path carries a major part of the reaction. The first- and second-order rate constants decrease as the basicity of the leaving amine increases and plots of log k^r_1 and log k^r_2 against the pK_a of the conjugate acids of the amines are parallel straight lines with a slope of −0.55. The equilibrium constants for these reactions have been determined from the ratio of the rate constants and a plot of log K against the pK_a of the amines is linear with a slope of 0.57.

Introduction

In a recent paper,[2] we reported the kinetics of the reversible displacement, by chloride, of the amine ligand trans to dimethyl sulfoxide in complexes of the type *cis*-[Pt(am)$_2$(DMSO)Cl]Cl, the amines being members of a series of primary alicyclic amines ranging from cyclopropylamine to cyclooctylamine. Although the original intention was to examine the way in which the lability of the complex related to the basicity of the leaving group, it was found that the other amine ligand produced a very strong cis effect that followed the same dependence on basicity as the leaving group effect and was almost as large. Complexes of this type with less basic amines were not stable enough to allow a satisfactory investigation of the leaving group effect over a sufficiently wide range of amine basicity and so, in order to extend the range and to maintain a constant cis effect, we turned our attention to the forward and reverse steps of the reaction

$$[PtCl_3(DMSO)]^- + am \underset{k^r}{\overset{k^f}{\rightleftarrows}} trans\text{-}[PtCl_2(am)(DMSO)] + Cl^- \qquad (1)$$

It was possible to prepare, characterize, and study the complexes of a wide range of primary, secondary, and heterocyclic amines covering a range of basicity $2.84 < pK_a < 8.66$ and to measure the rates of the forward reaction for a similar range of amines but covering the range $2.84 < pK_a < 11.12$.

Experimental Section

Preparations. Potassium trichloro(dimethyl sulfoxide)platinate(II) was prepared by two of the three methods reported by Kukushkin,[3] namely, (i) the action of KCl upon a suspension of *cis*-[Pt(DMSO)$_2$Cl$_2$] in water[4] and (ii) the reaction between equimolar

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[2] P. D. Braddock, R. Romeo, and M. L. Tobe, *Inorg. Chem.*, 13, 1170 (1974).

[3] Y. N. Kukushkin, Y. E. Vyazmenskii, and L. I. Zorina, *Russ. J. Inorg. Chem.*, 13, 1573 (1968).

[4] The original preparation called for equimolar amounts of the two reagents but this leaves a considerable amount of unreacted starting material. We found that a fourfold excess of KCl gave a better product.