970. *Pyrazine Metal Complexes. Part III.* Derivatives of Nickel*(II).

By A. B. P. LEVER, J. LEWIS, and R. S. NYHOLM.

A series of complexes of nickel(II) with pyrazine, methylpyrazine (Mp), 2,5- and 2,6-dimethylpyrazine, and tetramethylpyrazine is described. The magnetic and spectral properties have been utilised for stereochemical identification. The complexes fall into two main groups, planar diamagnetic compounds and octahedral spin-free paramagnetic compounds. The second group can be divided into two subsidiary groups based upon the mean value of *Dq*. For complexes involving a terminal pyrazine unit *Dq* falls in the region of 1000 cm.$^{-1}$, whilst for bridging pyrazine and/or sterically hindered pyrazine groups *Dq* falls in the region of 800 cm.$^{-1}$. The nature of some complexes of the general formula Mp_5NiX_2 is discussed; these are best regarded as octahedral nickel(II) complexes with one extra mol. of methylpyrazine of solvation.

A SERIES of complexes of nickel(II) with pyrazine and methylpyrazines has been prepared. The compounds are, in general, less soluble than corresponding cobalt derivatives [1] and tend to form polymeric structures in which the metal atom is octahedral. In contrast with the cobalt derivatives, no compound has been identified in which pyrazine is co-ordinated to a tetrahedral nickel atom. However, a number of diamagnetic, square-planar complexes have been prepared; it is noteworthy that no analogous cobalt derivative has been obtained. The octahedral complexes may be divided into two groups on the basis of their visible absorption spectra. The two groups have different values of *Dq*, the crystal-field parameter.

It is convenient to discuss the complexes in terms of the particular pyrazine ligand present.

Pyrazine.—Weakly coloured complexes of the general formula $(Pyz)_2NiX_2$ where X = Cl, Br, I, or NCS (Table 1) are prepared by direct interaction of pyrazine and the nickel salt at 100°. The paramagnetic omplexes are virtually insoluble in all solvents but decompose in hot water with dissociation of pyrazine groups.

Methylpyrazine.—Reaction of methylpyrazine (Mp) with alcoholic solutions of nickel salts leads to paramagnetic complexes of the type $MpNiX_2$, where X = Cl or Br, and Mp_2NiX_2, where X = I or NCS. These are paramagnetic and virtually insoluble in most solvents. Unlike the corresponding cobalt derivatives they show no tendency to give tetrahedral species in solution.

If these complexes, or the simple nickel salts, are recrystallised from boiling methylpyrazine, a new series of compounds is obtained, namely, Mp_5NiX_2 where X = Cl, Br, I, or NCS. If hydrated nickel chloride is used, the complex $Mp_4(H_2O)NiCl_2$, which cannot be dehydrated without concomitant loss of methylpyrazine, is formed; from acetone solution it is possible to prepare $Mp_4(acetone)NiI_2$. The chloro- and bromo-nickel(II) complexes of the type Mp_5NiX_2 are only slightly soluble in most solvents, but dissolve with dissociation in hot water. The iodo-complexes are more soluble but in the absence of an excess of methylpyrazine tend to rearrange to form the NiI_4^{2-} anion. The presence of this anion is indicated by its solution spectrum [2] and by the fact that the conductivity in acetone is 137 mho/mole for 0·0005M-solution. The complex $Mp_5Ni(NCS)_2$, is more readily soluble in various solvents and has a solution spectrum which depends critically on the solvent. Addition of an excess of methylpyrazine to a solution of the complex in some other solvent

---

* Part II, *J.*, 1963, 3156.

[1] (*a*) Lever, Lewis, and Nyholm, *J.*, 1962, 1235; (*b*) *Nature*, 1961, **189**, 58.

[2] Gill and Nyholm, *J.*, 1959, 3997.

TABLE 1.

Visible absorption spectra and magnetic moments of some pyrazine nickel(II) complexes.

Complex	Colour	Magnetic moment (μ_{eff} at 298°K)	Visible absorption spectra (mμ) (ε in parentheses)				
Octahedral (*group* A)							
$Pyz_2Ni(NCS)_2$	Pale blue	3·21			600 ‡		960
Pyz_2NiCl_2	Pale green	3·18			620 ‡	820sh	950
Pyz_2NiBr_2	Pale green	3·13			635 ‡		960
Pyz_2NiI_2	Yellow	3·14			640 ‡		940
$Mp_5Ni(NCS)_2$	Blue	3·24			600 ‡	795sh	960
			367(287) §		590(13·2)	780(4·5)	955(16)
			349(28) ¶	395(16)	665(6·5)	795s(2·6)	
			360(143) ‖		625(14·2)		
Mp_5NiCl_2	Yellow-green	3·30	375(282) §		640(6·6)	810(1·8)	
Mp_5NiBr_2	Yellow-green	3·24	375(294) §		640(8·7)	825(2·9)	
Mp_5NiI_2	Yellow	3·19	400(5180) §		647(9·4)		
$Mp_2Ni(NCS)_2$	Pale blue	3·26			625 ‡	780sh	960
$(2,6\text{-}Dmp)_4Ni(NCS)_2$	Blue	3·22			600 ‡		960
			355(143) ‖		630(11·5)	844sh(4·4)	
$(2,6\text{-}Dmp)_2Ni(NCS)_2$	Pale blue	3·11			620 ‡		960
Octahedral (*group* B)							
$MpNiCl_2$ *	Pale green	3·42	435sh ‡	760	800sh	840sh	
$MpNiBr_2$ *	Pale blue	3·37	435sh ‡	745b			
Mp_2NiI_2	Brown	3·26		735sh ‡	770		
$(2,6\text{-}Dmp)_2NiCl_2$	Pale green	3·38	420 ‡	740b	825sh		
$(2,6\text{-}Dmp)_2NiBr_2$	Pale blue	3·32	432sh ‡	740b			
$(2,5\text{-}Dmp)NiCl_2$ *†	Pale yellow	3·4	440 ‡	770		850	
Square-planar							
$(2,5\text{-}Dmp)NiBr_2$ *	Purple	0	385sh ‡	585		860	
$(2,5\text{-}Dmp)NiI_2$ *	Black	0	450 ‡	640			
$(2,6\text{-}Dmp)NiI_2$ *	Black	0	427 ‡	645b		875	
Tmp_2NiI_2	Deep green	0	410 ‡	657			

Pyz = pyrazine; Mp = methylpyrazine; 2,5-Dmp = 2,5-dimethylpyrazine; 2,6-Dmp = 2,6-dimethylpyrazine; Tmp = tetramethylpyrazine.

* Bridging through pyrazine units. † Isomorphous with corresponding cobalt compounds. ‡ Diffuse reflectance spectrum. Solvents for absorption spectra: § methylpyrazine; ¶ methanol; ‖ acetone. sh = Shoulder. b = Broad.

gives a spectrum identical with that of methylpyrazine itself and identical with the diffuse reflectance spectrum of the solid.

It is evident from this observation that some dissociation occurs in solution. When solutions of the complex, in other than methylpyrazine, are heated or are set aside in the cold for some time, a precipitate of a compound $Mp_2Ni(NCS)_2$ is obtained. This dissociation precludes a molecular-weight determination but the complex and its analogues are presumed to be monomeric. The complex $Mp_5Ni(NCS)_2$ is a non-electrolyte in acetone (19 mho/mole; 0·0005M) * and the solid has an infrared spectrum indicative of terminal thiocyanate groups bonded through nitrogen[3] (see Table 2). If strongly heated, these pentakis-compounds lose methylpyrazine, yielding the mono- or bis-methylpyrazine derivatives described above.

2,5-Dimethylpyrazine.—Direct reaction of the ligand (2,5-Dmp) with nickel salts leads to complexes of the form $(2,5\text{-}Dmp)NiX_2$ where X = Cl, Br, or I. However, whereas the chloride is similar in type to the corresponding methylpyrazine derivative, being paramagnetic, weakly coloured, and insoluble in most solvents, the bromide and iodide are intensely coloured and diamagnetic (Table 1). The iodide dissociates to NiI_4^{2-} in solution, as indicated by its absorption spectrum; the bromide is of low solubility, but may be

---

* A 1 : 1 electrolyte in acetone has a molar conductance of the order of 120 mho/mole.

[3] Lewis, Nyholm, and Smith, *J.*, 1961, 4590.

TABLE 2.

Principal infrared absorption bands (3—15 μ) (in cm.$^{-1}$).

(Italicised maxima are held to characterise bonding by one nitrogen atom only. Maxima in heavy type arise from vibrations in the thiocyanate group.)

All pyrazinenickel complexes: 1720 ± 5w; 1403 ± 7w; 1295 ± 5vw-w; 1150 ± 3s; 1110 ± 4vs; 1052 ± 6vs. Also as follows:

$Pyz_2Ni(NCS)_2$	**2075**vs	**2020**sh	*971*m	*964*m	809s	801s	**788**s
Pyz_2NiCl_2	*937*m	821s	814s				
Pyz_2NiBr_2	*987*m	821s	817s				
Pyz_2NiI_2	*986*m	818s	731w	722s			

All methylpyrazinenickel complexes: 1600 ± 15w-m; 1505 ± 15w-m; 1403 ± 7w; 1305 ± 6m; 1300 ± 2m; 1173 ± 3s; 1074 ± 10s; 1041 ± 6w-m; 734 ± 8s; 720 ± 1s. Also as follows:

$MpNiCl_2$	1026s						
$MpNiBr_2$	1029s	816m					
Mp_2NiI_2	1644w	*1261*m	1176m	1044m	831w	821vs	
$Mp_2Ni(NCS)_2$	**2121**vs	*1248*vw	**781**m				
$Mp_5Ni(NCS)_2$	**2062**vs	*1248*m	1054w	835vs	**804**s		
$Mp_4(H_2O)NiCl_2$	*1248*m	1036m	849s	840s	826sh		
Mp_5NiBr_2	1653m	1587m	*1246*m	1035s	851m	844m	
Mp_5NiI_2	1642w	*1248*m	1053w	939w	851m	838m	824w
$Mp_4(Acetone)NiI_2$	1705s *	1610m	*1250*m	1212m	935w	852sh	837vs

All 2,5-dimethylpyrazinenickel complexes: 1495 ± 5ms; 1350 ± 2m; 1243 ± 3w; 1163 ± 5vs; 1026 ± 5m; 983 ± 3m. Also as follows:

$(2,5\text{-}Dmp)NiCl_2$	1389sh	1325m	1271w	1070s	966m	887s	719m
$(2,5\text{-}Dmp)NiBr_2$	1534w	877s	862m	826w	731m	720m	
$(2,5\text{-}Dmp)NiI_2$	1420m	870vs	758w				

All 2,6-dimethylpyrazinenickel complexes: 1424 ± 6sh; 1173 ± 2 ms; 1022 ± 4*s*; 946 ± 7w-m; 735 ± 5s; 725 ± 5sh. Also as follows:

$(2,6\text{-}Dmp)_2NiCl_2$	1536w	1284w	*1164*s	860s							
$(2,6\text{-}Dmp)_2NiBr_2$	1536m	1418m	1284w	*1164*s	949w	863s	720sh				
$(2,6\text{-}Dmp)_2Ni(NCS)_2$	**2114**vs	1538m	1420w	1250s	*1161*s	864s	*777*m				
$(2,6\text{-}Dmp)_4Ni(NCS)_2$	**2070**vs	**2024**sh	1568m	1531m	1378w	1285m	1252s	*1160*s	875vs	**813**m	738s
$(2,6\text{-}Dmp)NiI_2$	1505m	1362m	990w	856s							
Tmp_2NiI_2	1316m	1350m	1230m	1171s	993s	813s	747s				

* Ketone frequency.

purified by extraction (Soxhlet) with dry acetonitrile or acetone, in which solvents it gives a blue solution.

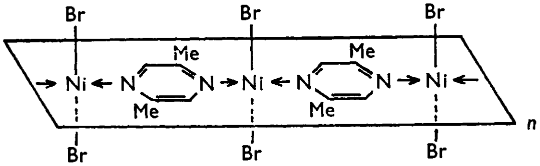
2,6-*Dimethylpyrazine* (2,6-Dmp).—The complexes $(2,6\text{-}Dmp)_2NiX_2$ (X = Cl, Br, or NCS), and $(2,6\text{-}Dmp)NiI_2$ are prepared in the normal manner. Recrystallisation of the thiocyanate from acetone in the presence of an excess of 2,6-dimethylpyrazine yields a material $(2,6\text{-}Dmp)_4Ni(NCS)_2$. Like the analogous cobalt complexes they are fairly soluble and with the exception of the iodide may be recrystallised from alcohol. The corresponding cobalt complexes[1] give blue solutions in acetone and probably exist therein as tetrahedral species. The nickel complexes are far less soluble in acetone but a boiling suspension of the bromide is faintly blue. The chloride, bromide, and thiocyanate complexes are paramagnetic with a moment indicating two unpaired electrons, and they are weakly coloured whilst the iodide is black and diamagnetic.

Tetramethylpyrazine (Tmp).—Tetramethylpyrazine does not react with nickel chloride, bromide, or thiocyanate either directly or in any of the solvents investigated. Addition of tetramethylpyrazine to solutions of these salts in alcohol did not alter the visible spectrum of the nickel ion, indicating absence of reaction in solution.

Nickel iodide, on the other hand, reacts fairly rapidly with tetramethylpyrazine in acetone, giving a deep-green crystalline precipitate, $(Tmp)_2NiI_2$. This diamagnetic product decomposes, yielding the NiI_4^{2-} ion in solution, and the crystals themselves lose their lustre when kept in a desiccator.

Discussion.—The diamagnetic complexes constitute one group, but the paramagnetic complexes may be divided into two groups on the basis of their visible spectra (Table 1). It is convenient to discuss the diamagnetic complexes first.

Diamagnetic complexes. The diffuse reflectance spectra do not allow us to distinguish between a square-planar and a tetrahedral configuration since both can give rise to intense absorption in the 600 mμ region.[2,4] The diamagnetism indicates a square-planar species but the colour is then difficult to explain since square-planar nickel derivatives are generally yellow or red. To resolve the difficulty an *X*-ray study of dibromo-(2,5-dimethylpyrazine)-nickel(II) was carried out by Ayers, Robertson, and Pauling.[5] The complex was found to have a polymeric square-planar arrangement about the nickel ion, with the bromine atoms rotated 90° out of the plane of the 2,5-dimethylpyrazine ligand (see I). This rotation reduces the steric interaction between the bromine atoms and the methyl groups. We may assume that all the diamagnetic pyrazine complexes have a square-planar arrangement of a similar type with the halogen atoms in a plane perpendicular to that of the pyrazine ligand. Steric interaction between methylpyrazines and halogens attached to the metal may be reduced either by rotation of the pyrazine ligand in the manner discussed, or by a change in stereochemistry to tetrahedral symmetry. The complexes reported here are diamagnetic and planar. A related compound, dibromobis-2-methylpyridine-nickel(II) has been reported as paramagnetic and tetrahedral.[6] It is not obvious at this stage what factors influence these alternatives, but lattice-energy effects may be important as there is very often a change in stereochemistry on dissolution. We might have expected a complex, $MpNiBr_2$, which is polymerised through the pyrazine ligand, to be diamagnetic and square; instead it is octahedral. It seems that there is only a small free-energy difference between a possibly four-co-ordinate square form and six-co-ordinate, perhaps distorted octahedral form.



(I)

Paramagnetic complexes. There is a clear division of the complexes into two series according to whether the main absorption band in the visible region is near 600 mμ (group A) or near 750 mμ (group B). An analysis of the spectra will be discussed elsewhere.[7] We conclude that both series contain octahedral nickel, the first with $Dq \sim 1000$ cm.$^{-1}$ and the second with $Dq \sim 800$ cm.$^{-1}$. We have already pointed out that it is possible to distinguish between a pyrazine bonded at one nitrogen atom [1,8] and the ligand bonded at both nitrogen atoms by means of the infrared spectra of the complexes. In this way we have deduced that all the complexes in group A have terminal pyrazine units (see Table 2). The second group contains examples of both terminal and bridging pyrazine units (see Fig. 3 of ref. 1(*b*)). The infrared spectra of polymers containing bridging pyrazine units are virtually identical with those of the corresponding binuclear cuprous derivatives.[8]

There are two mechanisms which may influence the *Dq* of the pyrazine ligand. (*a*) The *Dq* of a bridging ligand is expected to differ from that of a terminal one, and (*b*) steric interaction of a substituent in the α-position of the pyrazine group and other groups in the complex may lead to a change in the *Dq*. Both the pink compound $(Pyz)_2CoCl_2$ and the blue compound $(Pyz)CoCl_2$ are octahedral.[9] The infrared spectra indicate that in the former the pyrazine group is terminal whereas in the latter it acts as a bridge. Analysis of the

---

[4] Holm, *J. Amer. Chem. Soc.*, 1960, **82**, 5632.
[5] Ayers, Robertson, and Pauling, personal communication.
[6] Glonek, Curran, and Quagliano, *J. Amer. Chem. Soc.*, 1962, **84**, 2014.
[7] Lever, Lewis, and Nyholm, unpublished results.
[8] Lever, Lewis, and Nyholm, *J.*, 1963, 3156.
[9] Friesen, Lever, Lewis, and Nyholm, unpublished results.

spectra indicates that *Dq* of the ligand for the bridging group is lower than that of the terminal group. The more basic nitrogen in a substituted pyrazine will be that *ortho* to one or more methyl groups, *i.e.*, the potential donor site. For steric reasons, however, we may expect bonding at the unhindered nitrogen atom when (*a*) there is a large anion such as sulphur attached to the nickel or (*b*) a large number of pyrazine groups are associated with the metal ion. The presence of an α-methyl substituent may, however, lead to a longer Ni–N bond and hence to a lower *Dq*.

It is now possible to divide the compounds into group A and group B on this basis. The bridging complexes must involve bonding to a hindered nitrogen atom and hence belong to group B; pyrazine complexes having no substituent in the position α to the bonding nitrogen atom such as $(2,6\text{-Dmp})_4\text{Ni(CNS)}_2$ and the Mp_5NiX_2 series belong to group A. The complex, $\text{Mp}_2\text{Ni(CNS)}_2$, that forms bridges through the thiocyanate group, involves two sulphur–nickel bonds and hence belongs to group A. In the remaining compounds in group B the distortion is not sufficient to cause bonding through the unhindered position.

The pentakis(methylpyrazine) derivatives represent an interesting group. We have reported [1] the preparation of Mp_4CoCl_2 but were unable to prepare the corresponding bromide and iodide complex. It has since been observed [9] that cobalt thiocyanate and methylpyrazine readily give the compound $\text{Mp}_5\text{Co(NCS)}_2$ which is isomorphous with the nickel derivative and a non-electrolyte in acetone (it has been obtained independently by Nelson.[10]) The solid has a reflectance spectrum typical of octahedral cobalt. We conclude that the complexes are octahedral monomers, the fifth methylpyrazine molecule solvating the crystal. This unbonded methylpyrazine may be replaced by other solvents such as acetone or water (Table 1): for the acetone solvate the observed ketone frequency is closely similar to that of free acetone. Nelson,[10] in a thermogravimetric analysis of the material $\text{Mp}_5\text{Co(NCS)}_2$ observed loss of three methylpyrazine units to form initially a compound $\text{Mp}_2\text{Co(NCS)}_2$, without an intermediate $\text{Mp}_4\text{Co(NCS)}_2$. With the acetone and the aquo-complex we have been unable to remove the extra acetone or water molecule without at the same time removing methylpyrazine and it is thus possible that the complexes are seven co-ordinate. Although seven-co-ordinate first-row transition-metal complexes are known, *e.g.*, Mn^{II}(EDTA) and Fe^{III}(EDTA),[11] the spectra of our pyrazine complexes are readily interpretable in terms of octahedral symmetry; the spectra are similar to those of Pyz_2NiX_2 complexes where it is difficult to conceive of seven-fold co-ordination.

EXPERIMENTAL

Carbon and hydrogen analyses were carried out by Mr. A. Winter of this Department, and the nitrogen analyses by the Oxford Microanalytical Laboratory.

Dithiocyanatodipyrazinenickel(II).—Pyrazine (2 mol.), dissolved in a small volume of alcohol was added to an alcoholic solution of disodium tetrathiocyanatonickelate(II) (1 mol.). A dense, pale blue precipitate was formed instantly. The *product*, obtained in high yield, was purified by extraction (Soxhlet) with water (Found: C, 35·8; H, 2·9; N, 24·6; Ni, 17·4. $\text{C}_{10}\text{H}_8\text{N}_6\text{NiS}_2$ requires C, 35·8; H, 2·4; N, 25·1; Ni, 17·5%).

Dichlorodipyrazinenickel(II).—Stoicheiometric quantities of hydrated nickel chloride and pyrazine were mixed in ethanol. An almost quantitative yield of pale green product was obtained. The *compound* was purified by dissolving it in aqueous ammonia and acidifying this solution with hydrochloric acid. Crystals were obtained by keeping the solution overnight in a refrigerator. Difficulty was experienced in obtaining an accurate analysis (Found: Cl, 25·2; N, 19·3. $\text{C}_8\text{H}_8\text{Cl}_2\text{N}_4\text{Ni}$ requires Cl, 24·5; N, 19·3%).

Dibromodipyrazinenickel(II).—A mixture of nickel bromide (3 g.) and sodium bromide

---

[10] Nelson, personal communication.

[11] Hoard, Smith, and Lind, "Advances in the Chemistry of Coordination Compounds," ed. Kirschner, Macmillan & Co., New York, 1961, p. 296.

(10 g.) was dissolved in hot water (20 ml.). To the hot solution was added pyrazine (3·5 g.) in water (5 ml.). The solution was diluted with an equal volume of ethanol and placed in a refrigerator. Pale green crystals (5 g., 96%) were obtained. This *complex* was recrystallised from aqueous ammonia and hydrobromic acid (cf. the chloro-complex) (Found: C, 25·0; H, 2·2; Br, 41·6; N, 14·6; Ni, 15·0. $C_8H_8Br_2N_4Ni$ requires C, 25·4; H, 2·1; Br, 42·2; N, 14·8; Ni, 15·5%).

Di-iododipyrazinenickel(II).—Pyrazine (2 mol.) was added to an aqueous nickel chloride (1 mol.) solution containing a large excess of sodium iodide. The immediate orange precipitate of the *iodo-complex* (insoluble in aqueous ammonia) was recrystallised from water containing sodium iodide (Found: I, 53·3; N, 11·8; Ni, 11·8. $C_8H_8I_2N_4Ni$ requires I, 53·7; N, 11·9; Ni, 12·4%).

Dichloro(methylpyrazine)nickel(II).—Crushed nickel chloride hexahydrate was moistened with a slight excess of methylpyrazine and kept at 100° for ½ hr. The solid *product* was filtered off and twice extracted (Soxhlet) with ethanol (Found: Cl, 31·2; N, 12·2; Ni, 25·7. $C_5H_6Cl_2N_2Ni$ requires Cl, 31·6; N, 12·5; Ni, 26·3%).

Dibromo(methylpyrazine)nickel(II).—Prepared as was the chloro-complex, but by using nickel bromide), this *polymer* was not readily purifiable (Found: Br, 50·4; N, 9·2; Ni, 18·1. $C_5H_6Br_2N_2Ni$ requires Br, 51·1; N, 9·0; Ni, 18·8%).

Dichloropentakismethylpyrazinenickel(II).—Dichloro(methylpyrazine)nickel(II) was recrystallised twice from methylpyrazine that had been dried azeotropically. The *product*, after being washed with ether, was dried in a desiccator (Found: C, 50·4; H, 5·4; Cl, 12·4. $C_{25}H_{30}Cl_2N_{10}Ni$ requires C, 50·0; H, 5·0; Cl, 11·8%).

Dichloroaquotetrakismethylpyrazinenickel(II).—Nickel chloride hexahydrate was recrystallised twice from methylpyrazine. The *product* was washed with ether and dried in a desiccator (Found: Cl, 13·5; Ni, 10·8. $C_{20}H_{26}Cl_2N_8NiO$ requires Cl, 13·5; Ni, 11·2%).

Dibromopentakismethylpyrazinenickel(II).—Dibromomethylpyrazinenickel(II) was recrystallised several times from dry methylpyrazine; the product was washed with ether, and dried in a desiccator (Found: C, 43·8; H, 4·3; Br, 23·2; Ni, 8·7. $C_{25}H_{30}Br_2N_{10}Ni$ requires C, 43·6; H, 4·4; Br, 23·2; Ni, 8·5%).

Di-iodopentakismethylpyrazinenickel(II).—Prepared as was the bromide, but by using nickel iodide, this *complex* was dried in a desiccator (Found: I, 32·2; Ni, 7·1. $C_{25}H_{30}I_2N_{10}Ni$ requires, I, 32·4; Ni, 7·5%).

Di-iodo(acetone)tetrakismethylpyrazinenickel(II).—Nickel iodide (2 g.), dissolved in acetone (50 ml.) containing methylpyrazine (3 ml.), was refluxed for 1 hr. The solution, when left overnight in a refrigerator, deposited large yellow-green crystals of the *solvate* (2 g., 42%). These were recrystallised from acetone containing a few drops of methylpyrazine, washed with ligroin, and dried in a desiccator (Found: C, 37·8; H, 4·4; I, 34·5; Ni, 7·85. $C_{23}H_{30}I_2N_8NiO$ requires C, 38·3; H, 4·1; I, 34·0; Ni, 7·9%).

Di-iodobismethylpyrazinenickel(II).—The above acetone complex was heated at 130°/15 mm. for 2 hr., giving the new *complex* (Found: C, 24·0; H, 2·7; I, 50·7; Ni, 11·85. $C_{10}H_{12}I_2N_4Ni$ requires C, 23·9; H, 2·4; I, 50·7; Ni, 11·7%).

Dithiocyanatopentakismethylpyrazinenickel(II).—Methylpyrazine (5 ml.) was added to an alcoholic solution (50 ml.) of disodium tetrathiocyanatonickelate(II) (6 g.). The solution became deep blue and deposited blue crystals (6·4 g., 55%). This *product* was recrystallised twice from methylpyrazine, washed with ether, and dried in a desiccator (Found: C, 50·5; H, 5·3; N, 25·6; NCS, 17·8; Ni, 9·1; S, 10·2. $C_{27}H_{30}N_{12}NiS_2$ requires C, 50·2; H, 4·7; N, 26·0; NCS, 18·0; Ni, 9·1; S, 9·9%).

Dichloro-(2,5-dimethylpyrazine)nickel(II).—Nickel chloride hexahydrate (3 g.) and 2,5-dimethylpyrazine (7·5 ml.) were heated together at 100° for ½ hr. The liquid changed to a white "cream." This (2·4 g., 80%) was extracted (Soxhlet) with ethanol, and the solid *product* was dried at 50°/15 mm. (Found: C, 30·4; H, 3·5; Cl, 29·4; Ni, 25·1. $C_6H_8Cl_2N_2Ni$ requires C, 30·3; H, 3·4; Cl, 29·8; Ni, 24·8%).

Dibromo-(2,5-dimethylpyrazine)nickel(II).—Nickel bromide (3 g.) and 2,5-dimethylpyrazine (5 ml.) were heated together at 100° for ½ hr. The yellow salt rapidly became purple. Ether was added and the solid product (4·5 g., 100%) was filtered off and dissolved in a small volume of hot ethanol containing a few drops of 2,5-dimethylpyrazine (the solution so formed was yellow). Solvent was removed at the pump until the solution became purple and deposited purple crystals. Alternatively the crude product was recrystallised by extraction (Soxhlet) with dry acetonitrile, care being taken to exclude moisture. The product was dried at 50°/15 mm. and stored in a desiccator (Found: C, 22·6; H, 2·8; Br, 48·2; Ni, 17·6. $C_6H_8Br_2N_2Ni$ requires C, 22·1; H, 2·8; Br, 48·9; Ni, 18·0%). This *complex* readily absorbs water from the atmosphere, forming a pale green *heptahydrate* (Found: C, 15·9; H, 4·8. $C_6H_8Br_2N_2Ni,7H_2O$ requires C, 16·2; H, 4·5%).

Di-iodo-(2,5-*dimethylpyrazine*)*nickel*(II).—2,5-Dimethylpyrazine (3 ml.) was added to a solution of nickel iodide (2 g.) in acetone (50 ml.), and the mixture was refluxed for ¼ hr. Black crystals (1·5 g., 56%) were deposited rapidly from the boiling solution; this *complex* was collected, washed with hot ethanol, and dried at 50°/15 mm. (Found: I, 61·0; Ni, 13·8. $C_6H_8I_2N_2Ni$ requires I, 60·3; Ni, 14·0%).

Dichloro-(2,6-*dimethylpyrazine*)*nickel*(II).—Nickel chloride hexahydrate (3 g.) and 2,6-dimethylpyrazine (4 g.) were crushed together and heated at 100° for ¼ hr. Ether was then added and the *product* (2·9 g., 97%) filtered off, recrystallised from ethanol–ether, and dried at 50°/15 mm. (Found: C, 42·4; H, 5·2; Cl, 20·4; N, 15·9; Ni, 17·0. $C_{12}H_{16}Cl_2N_4Ni$ requires C, 41·6; H, 4·7; Cl, 20·5; N, 16·2; Ni, 17·0%).

*Dibromobis-*2,6-*dimethylpyrazinenickel*(II).—Procedure as for the chloro-complex gave the *bromo-compound* (Found: C, 33·7; H, 4·1; Br, 36·5; Ni, 13·1. $C_{12}H_{16}Br_2N_4Ni$ requires C, 33·1; H, 3·7; Br, 36·7; Ni, 13·5%).

Di-iodo-(2,6-*dimethylpyrazine*)*nickel*(II).—An acetone solution of 2,6-dimethylpyrazine (3 g. in 10 ml.) was added to a solution of nickel iodide (2 g.) in acetone (25 ml.), and the mixture was refluxed for ½ hr. The solution was filtered hot, yielding the *iodo-compound* as a black crystalline residue (0·67 g., 30%). This was purified by leaching it with hot acetone (Found: I, 60·0; N, 6·8; Ni, 13·9. $C_6H_8I_2N_2Ni$ requires I, 60·3; N, 6·7; Ni, 14·0%).

*Dithiocyanatotetrakis-*2,6-*dimethylpyrazinenickel*(II).—2,6-Dimethylpyrazine (2·4 g.) was added to an ethanol solution (30 ml.) of disodium tetrathiocyanatonickelate(II) (1·2 g.). The solution was refluxed for 5 min. and on cooling yielded pale blue crystals (1·76 g.). These were recrystallised from ethanol containing an equivalent quantity of 2,6-dimethylpyrazine to suppress dissociation. The *complex* was dried in a desiccator (Found: C, 50·9; H, 5·2; NCS, 19·0; Ni, 9·65. $C_{26}H_{32}N_{10}NiS_2$ requires C, 51·4; H, 5·3; NCS, 19·1; Ni, 9·7%).

Dithiocyanatobismethylpyrazinenickel(II).—The complex $Mp_5Ni(NCS)_2$ was suspended in boiling ether for 1 hr. The product was filtered off and the process repeated with a fresh volume of ether. The resulting *complex* was dried at 100°/15 mm. (Found: C, 40·2; H, 3·0; NCS, 31·5; Ni, 15·9. $C_{12}H_{12}N_6NiS_2$ requires C, 39·7; H, 3·3; NCS, 32·0; Ni, 16·2%).

A similar procedure gave *dithiocyanatobis-*2,6-*dimethylpyrazinenickel*(II) (Found: NCS, 29·2; Ni, 14·7. $C_{14}H_{16}N_6NiS_2$ requires NCS, 29·7; Ni, 15·0%).

Di-iodobistetramethylpyrazinenickel(II).—Tetramethylpyrazine (4 g.) in acetone (10 ml.) was added to a filtered solution of nickel iodide (2 g.) in acetone (25 ml.). The brown mixture was set aside for 24 hr. during which green crystals (1·3 g., 53%) were deposited. This *product* was washed with a little cold acetone containing some tetramethylpyrazine and dried in a desiccator. The green crystals lose their lustre and decompose in a few weeks (Found: C, 32·9; H, 4·35; I, 43·5; N, 9·6; Ni, 10·1. $C_{16}H_{24}I_2N_4Ni$ requires C, 32·8; H, 4·1; I, 43·4; N, 9·6; Ni, 10·0%).

The authors are indebted to the Wyandotte Chemical Corporation, Michigan, U.S.A., for the supply of pyrazines and for financial assistance (to A. B. P. L.).

WILLIAM RAMSAY AND RALPH FORSTER LABORATORIES,
UNIVERSITY COLLEGE, GOWER STREET,
LONDON W.C.1.

[*Received, March* 11*th*, 1963.]