

THE STRUCTURE OF
TRIAQUO[2,6-DI(2'-PYRIDYL)-4-(PYRIDINIUM-2'-YL
BROMIDE)-1,3,5-TRIAZINE]NICKEL(II) BROMIDE MONOHYDRATE

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In the course of our investigations¹⁻³ on the terdentate ligand 2,4,6-tri(2'-pyridyl)-1,3,5-triazine (tpt, $C_{18}H_{12}N_6$) a crystalline compound of general formula $C_{18}H_{21}Br_3N_6NiO_4$ was isolated. We have determined the structure of this bivalent nickel chelate by consideration of spectroscopic measurements in the visible and infrared regions, a magnetic susceptibility measurement, thermogravimetric studies, and X-ray diffraction techniques.

The complex was prepared by the reaction of the ligand with a warm acidic aqueous solution of nickel (II) bromide. The product crystallized from the solution in amber-green octagonal plates. An analysis for carbon, hydrogen, and nitrogen suggested the formulation above. A thermogravimetric study showed the compound to be a tetrahydrate, as evidenced by a weight loss equivalent to 4 moles of water per mole of complex over the temperature range 100–200°. Further heating to 250° caused a loss of weight equivalent to one mole of hydrogen bromide. The brown solid remaining proved to be the compound $[NiBr_2 \text{ tpt}]$ which had been previously characterized.¹

It has been suggested in earlier papers^{1,4} that in this hydrobromide type of complex the ligand is present in a form where the nitrogen atom of the uncoordinated pyridyl group is protonated. The release of hydrogen bromide from the complex upon heating supports this suggestion. However, the nature of the coordination sphere around the nickel atom to this point was not completely established. Whilst the solid state spectrum (Fig. 1) and a room temperature magnetic moment of 3.0 B.M. both suggest octahedral coordination, presumably with the ligand acting as a terdentate, it was not clear whether the other three coordination sites were occupied by water molecules, bromine atoms, or some combination of both. It was therefore decided to attempt a complete structural analysis by single-crystal X-ray diffraction methods.

$[Ni(H_2O)_3(\text{tpt}, HBr)]Br_2 \cdot H_2O$ crystallizes in the monoclinic system, with space group $P2_1$, and with two molecules in the unit cell of dimensions: a 12.04, b 11.20, c 8.97 Å, and β 96.5°. At the present stage of refinement (R 0.097) the positions of all the Ni, Br, O, N, and C atoms have been determined. A simplified structure of the compound is represented in Figure 2.

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¹ Vagg, R. S., Warrener, R. N., and Watton, E. C., *Aust. J. Chem.*, 1967, **20**, 1841.

² Vagg, R. S., Warrener, R. N., and Watton, E. C., *Aust. J. Chem.*, 1969, **22**, 141.

³ Vagg, R. S., M. Sc. Thesis, University of New South Wales, 1966.

⁴ Collins, P. F., Diehl, H., and Smith, G. F., *Analyt. Chem.*, 1959, **31**, 1862.

It is of interest to note that all four aromatic rings in the ligand are coplanar. This coplanarity is enforced in two of the pyridyl rings and the triazine ring by virtue of their coordination to the nickel atom, but the reason for the coplanarity of the third protonated pyridyl ring is not obvious. A further interesting feature of that ring is the fact that the site of protonation, the nitrogen atom (N_P), may be verified by the

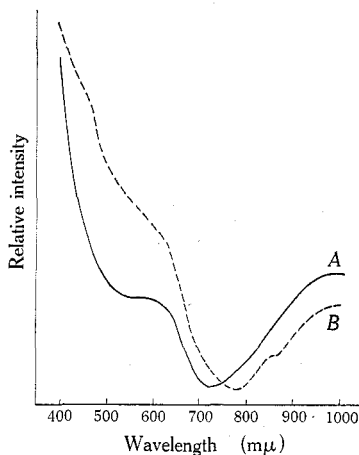
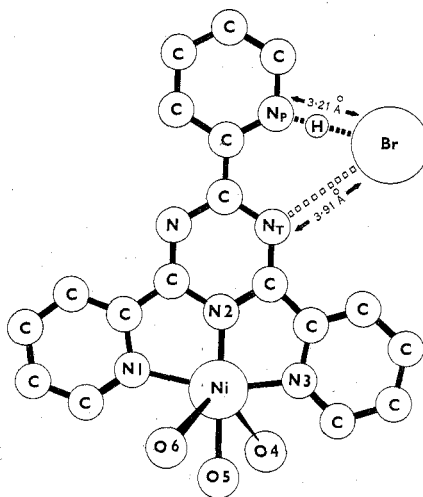


Fig. 1.—Solid state reflectance spectra of nickel (π) complexes.

A, $[\text{Ni}(\text{H}_2\text{O})_3(\text{tpt}, \text{HBr})]\text{Br}_2 \cdot \text{H}_2\text{O}$;

B, $\text{Ni}(\text{tpt}, \text{HBr})\text{Br}_2 \cdot 2\text{H}_2\text{O}$.

Fig. 2.—The structure of $[\text{Ni}(\text{H}_2\text{O})_3(\text{tpt}, \text{HBr})]\text{Br}_2 \cdot \text{H}_2\text{O}$.



position of one of the bromide ions, which presumably remains bonded to the proton and is thus incorporated essentially as a mole of HBr. The alternative possibility of the protonation of the triazine nitrogen atom (N_T) may be discounted after a consideration of the large N_P -Br interatomic distance of 3.91 \AA . The N_P -Br distance of 3.21 \AA , however, is the shortest N-Br interatomic distance in the crystal.

The nickel atom is in the centre of a distorted octahedron of one triazine and two pyridyl nitrogen atoms of the ligand and three water molecules. Details of the coordination sphere surrounding the nickel atom are given in Table 1.

The fourth water molecule and the other two bromide ions are dispersed throughout the crystal lattice. However, a close inspection of the positions of all the bromide ions and oxygen atoms reveals an apparent hydrogen-bonding network throughout the lattice between the bromide ions and the water molecules, which would account for the presence of broad absorption over the range 2500–3700 cm^{-1} of the compound's infrared spectrum. It is intended to refine the structure further with a view to determining the hydrogen atomic positions and hence confirming the existence of $\text{O-H}\cdots\text{Br}$ hydrogen bonding in the crystal. The final results, including a detailed report on the complete structural analysis, will be the subject of a subsequent publication.

TABLE 1
INTERATOMIC DISTANCES AND ANGLES IN NICKEL COORDINATION
SPHERE

Atoms	Dist. (Å)	Atoms	Angle
Ni-N 1	2.12	N 1-Ni-N 2	75.9°
Ni-N 2	2.10	N 2-Ni-N 3	77.3°
Ni-N 3	2.02	N 3-Ni-O 5	104.3°
Ni-O 4	2.08	O 5-Ni-N 1	103.4°
Ni-O 5	2.18	N 2-Ni-O 5	177.5°
Ni-O 6	2.09	N 1-Ni-N 3	152.3°
N 1-N 2	2.56	O 4-Ni-O 6	172.3°
N 2-N 3	2.57	O 4-Ni-O 5	85.9°
N 3-O 5	3.32	O 4-Ni-N 2	92.1°
O 5-N 1	3.37	O 6-Ni-N 2	94.8°
O 4-N 1	2.96	O 6-Ni-O 5	87.2°
O 4-N 2	3.01		
O 4-N 3	2.94		
O 4-O 5	2.90		
O 6-N 1	3.11		
O 6-N 2	3.08		
O 6-N 3	2.83		
O 6-O 5	2.94		

Another protonated compound similar to the one under discussion but containing two less water molecules had been prepared earlier.¹ In that compound the coordination of the nickel atom must be necessarily different, and this is confirmed by a comparison of the two solid state visible spectra shown in Figure 1. Dehydration of that compound also results in the production of the anhydrous form $[\text{NiBr}_2 \text{tpt}]$.

Acknowledgment

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