the unit cell volume of the tellurium scheelites is larger than that of the molybdenum scheelites, suggesting a larger ionic size of Te^{6+} than Mo^{6+}. From chemical analysis evidence which yields stoichiometric formulas, it seems that the charge compensation in $Sr_{0.9}Gd_{0.1}MoO_4$ and $Sr_{0.9}Eu_{0.1}MoO_4$ is achieved through the presence of some lower valent molybdenum. However, more physical measurements would be needed to ascertain this assumption. Table I also reports the unit cell dimensions of $Na_{0.5}Tm_{0.5}MoO_4$, whose growth conditions were apparently different from the other scheelites with similar composition. In the composition diagram Na_2O–Gd_2O_3–MoO_3 two fields are indicated[5] to produce large crystals. One field requires a higher and the other a lower heating temperature. Apparently, the Tm scheelite seems to prefer the higher temperature composition rather than the lower temperature mixtures. Figure 1 represents the unit cell volume of the different sodium rare earth scheelites *vs.* the empirical Goldschmidt radius of the rare earth ions. As expected one can see the volume contraction of the scheelite crystal with the increase of the atomic number of the rare earth ion.

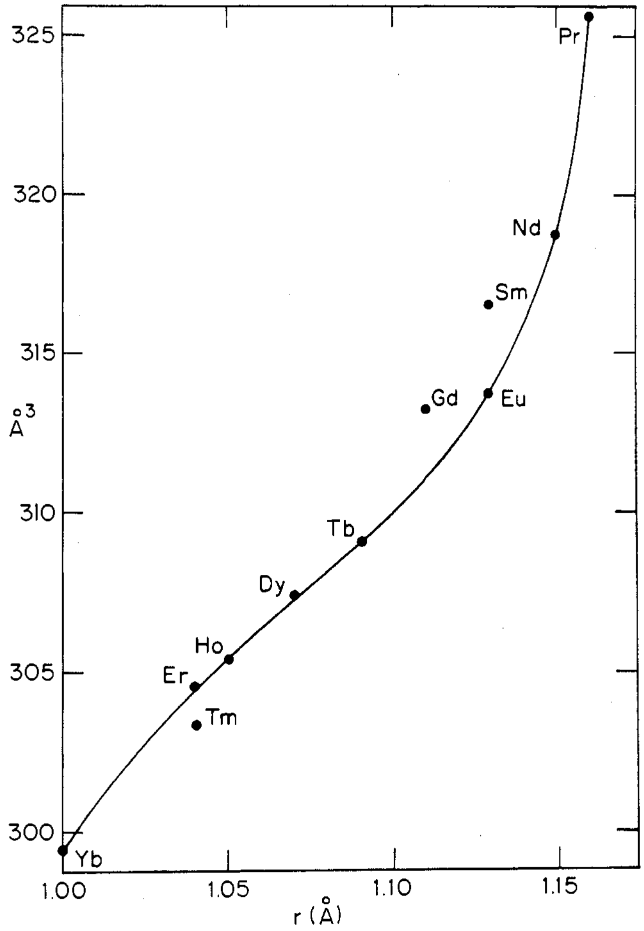

Figure 1.—Variation of the crystal volume in Å.^{3} with the Goldschmidt ionic radius of the rare earth ion M in the formula $Na_{0.5}M_{0.5}MoO_4$. The unit cell volume was calculated from the data published in ref. 5 except for $Na_{0.5}Pr_{0.5}MoO_4$ and $Na_{0.5}Tm_{0.5}MoO_4$, first reported in this note.

Acknowledgments.—The author wishes to acknowledge J. Siebel and S. Fisk for their technical assistance in the X-ray unit cell determination.

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The Magnetic Moments of Some Tetragonal Nickel Complexes

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Received December 18, 1964

Magnetic measurements have for some time been used to distinguish between the nickel ion in a tetrahedral or in an octahedral environment.[1] Octahedral nickel(II) complexes generally have temperature-independent magnetic moments within the range 2.9–3.3 B.M.; tetrahedral derivatives, on the other hand, have magnetic moments, which are temperature dependent, within the range 3.3–4.0 B.M. at 25°. Temperature range measurements are, however, rarely employed and single-temperature studies have been extensively used as a guide to the stereochemical environment of the nickel ion.

It is the purpose of this note to point out the existence of a class of tetragonal nickel complexes which have moments above 3.3 B.M.

Six-coordinate nickel complexes of the form *trans*-NiA_2X_2, where A is an amine and X a halogen, commonly have moments between 3.3 and 3.5 B.M. (Table I). The moments observed are not only outside the range generally associated with octahedral nickel derivatives, but are, in fact, higher than the theoretical maximum obtainable from the simple theory.

Gill and Nyholm[2] have calculated the magnetic moment values to be expected for the nickel ion in a variety of different circumstances (*e.g.*, zero or infinite spin–orbit coupling, very weak or very strong crystal fields, etc.) Although the moment can rise as high as 5.59 B.M. in the absence of an electrical field, they conclude that in an octahedral environment the magnetic moment should be 3.1–3.2 B.M.

Few temperature-range studies have as yet been carried out with the complexes listed in Table I,[3-10] but

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(2) N. S. Gill and R. S. Nyholm, *J. Chem. Soc.*, 3997 (1959).
(3) N. S. Gill, R. S. Nyholm, G. A. Barclay, T. I. Christie, and P. J. Pauling, *J. Inorg. Nucl. Chem.*, **18**, 88 (1961).
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(6) D. M. L. Goodgame and M. Goodgame, *ibid.*, 207 (1963).
(7) A. B. P. Lever, *J. Inorg. Nucl. Chem.*, **27**, 149 (1965).
(8) A. B. P. Lever, S. M. Nelson, and T. M. Shepherd, *Inorg. Chem.*, in press.
(9) W. Klemm and W. Schuth, *Z. anorg. allgem. Chem.*, **210**, 33 (1933).
(10) B. J. Hathaway and D. G. Holah, *J. Chem. Soc.*, 2400 (1964).

TABLE I

THE MAGNETIC MOMENTS OF SOME COMPLEXES NiA_2X_2

Complex[a]	μ,[b] B.M.	Ref.	Complex[a]	μ,[b] B.M.	Ref.
$Ni(py)_2Cl_2$	3.37	3	$Ni(IQuin)_2Br_2$	3.42	8
$Ni(py)_2Br_2$	3.35	4	$Ni(NH_3)_2Cl_2$	3.35	9
$Ni(\beta\text{-Pic})_2Cl_2$	3.45	4	$Ni(NH_3)_2Br_2$	3.29	9
$Ni(\beta\text{-Pic})_2Br_2$	3.25	4	$Ni(CH_3CN)_2Cl_2$	3.47	10
$Ni(\gamma\text{-Pic})_2Cl_2$	3.35	4	$Ni(CH_3CN)_2Br_2$	3.40	10
$Ni(\gamma\text{-Pic})_2Br_2$	3.34	4	$Ni(3\text{-Etpy})_2Cl_2$	3.37	8
$Ni(Mp)Cl_2$[c]	3.42	5	$Ni(3\text{-Etpy})_2Br_2$	3.40	8
$Ni(Mp)Br_2$[c]	3.37	5	$Ni(aniline)_2Cl_2$	3.36	8
$Ni(2,6\text{-Dmp})_2Cl_2$	3.38	5	$Ni(aniline)_2Br_2$	3.39	8
$Ni(2,6\text{-Dmp})_2Br_2$	3.32	5	$Ni(m\text{-Tol})_2Cl_2$	3.41	8
$Ni(2,5\text{-Dmp})Cl_2$[c]	3.4	5	$Ni(m\text{-Tol})_2Br_2$	3.39	8
$Ni(Quin)_2Cl_2$	3.41	6	$Ni(p\text{-Tol})_2Cl_2$	3.43	8
$Ni(Qx)_2Cl_2$	3.44	7	$Ni(p\text{-Tol})_2Br_2$	3.42	8
$Ni(Qx)_2Br_2$	3.43	7			
$Ni(IQuin)_2Cl_2$	3.40	8			

[a] py = pyridine; Pic = picoline; Mp = methylpyrazine; Dmp = dimethylpyrazine; Quin = quinoline; IQuin = isoquinoline; Qx = quinoxaline; Etpy = ethylpyridine; Tol = toluidine. [b] The moments were measured in the range 15–25°. [c] Bridging amine.

there is some evidence[11] that the magnetic moment, of some of the pyrazine complexes at least, actually increases slightly with decreasing temperature. This effectively precludes the possibility that the enhanced moments arise solely through a temperature-independent paramagnetic mechanism. The moments are independent of field strength, thus eliminating ferromagnetic phenomena. It appears, therefore, that the high moments may arise from a larger than normal orbital contribution, but at present there seems to be no reasonable mechanism to account for this.

The magnetic moment of an octahedral nickel complex is given,[1] to a first approximation, by

$$\mu_e = (4S(S+1))^{1/2}\left(1 - \frac{4\lambda}{\Delta E}\right)$$

where λ is the spin–orbit coupling coefficient and ΔE is the energy difference between the ground state and the first excited state ($10Dq$). In addition, there is a temperature-independent term arising from the second-order Zeeman effect[12]

$$\chi_{TIP} = \frac{8N\beta^2}{\Delta E} = \frac{2.09}{\Delta E}$$

The lowest value of ΔE likely to be experienced by the nickel ion in an octahedral environment is about 7000 cm.$^{-1}$ as in $CsNiBr_3$, which, assuming $\lambda = -240$ cm.$^{-1}$ (or about 75% of the free-ion value), leads to a moment of 3.33 B.M. (anhydrous nickel bromide has a magnetic moment of 3.25 B.M.[9] but is probably not magnetically dilute). Use of the free-ion value for λ leads to a magnetic moment of 3.45 B.M., but this upper limit would never be reached due to the known tendency for λ to be considerably reduced upon complex formation. Even if λ is as high as 85% of the free-ion value, $\mu = 3.39$ B.M. (for $\Delta E = 7000$ cm.$^{-1}$), which is below many of the values quoted in Table I obtained from complexes where the mean value of ΔE is likely to be considerably above 7000 cm.$^{-1}$. The practical limit for regular octahedral nickel derivatives may therefore be regarded as being about 3.33 B.M.

Although no X-ray analysis has been carried out on any of the compounds, $Ni(py)_2Cl_2$ is isomorphous[3] with violet $Co(py)_2Cl_2$, which has been shown[13] to have a polymeric six-coordinate structure involving chloride bridging and *trans* pyridine groups. The symmetry is C_{2h}. A similar structure is envisaged for all the compounds.

The absorption spectrum in the visible region[8] is typical for an octahedral nickel complex with a medium field ligand ($10Dq$ 7800–8600 cm.$^{-1}$), implying little splitting of the second and third excited states in the lower symmetry. There is some evidence, however, of broadening or splitting of the first electronic transition in the near-infrared,[7,10] indicating that the first excited state may be split appreciably. Such splitting might have been predicted to have given rise to a reduction rather than an enhancement of the orbital contribution.

Since most other nickel complexes of similar type, such as NiA_4X_2, have moments[4,5,14] within the normal octahedral range, it is possible that the high moment arises in some manner as a result of the presence of π-orbitals on the halogen atoms. Interaction of these filled orbitals with nickel filled $d\pi$-orbitals could conceivably reduce the energy separation between the ground state ($^3B_{1g}$)[15] and the first excited state (^3E_g) to a value below 7000 cm.$^{-1}$; there is some spectroscopic evidence that this does occur in the acetonitrile complexes.[10] However, this implies a mixing of the ligand and d electrons and will result in a loss of orbital angular momentum by an amount proportional to k, the orbital delocalization factor.[16] Such a mechanism therefore does not seem to be very useful unless k can be assumed to be near 1, which is unlikely. It is hoped that a possible mechanism will arise when detailed measurements have been made with these complexes over a temperature range. In the meantime it is pertinent to point out the danger which exists in assigning a tetrahedral stereochemistry to nickel complexes with moments above 3.3 B.M. unless there is good alternative evidence to support such a conclusion.[17]

Acknowledgment.—The author is indebted to Professor J. Lewis for useful discussions.

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[11] A. B. P. Lever, J. Lewis, and R. S. Nyholm, unpublished observations.

[12] B. N. Figgis, *Trans. Faraday Soc.*, **56**, 1553 (1960).

[13] J. D. Dunitz, *Acta Cryst.*, **10**, 307 (1957).

[14] S. Buffagni, L. M. Vallerino, and J. V. Quagliano, *Inorg. Chem.*, **3**, 671 (1964).

[15] Although the crystal symmetry is C_{2h}, it is probable that the effective symmetry at the metal atom is D_{4h}.

[16] C. J. Ballhausen, "Introduction to Ligand Field Theory," McGraw-Hill Book Co., New York, N. Y., 1962.

[17] NOTE ADDED IN PROOF.—Recently (D. M. L. Goodgame, M. Goodgame, and M. J. Weeks, *J. Chem. Soc.*, 5194 (1964)) the magnetic moments of certain of these complexes have been shown to increase with decreasing temperature. A ferromagnetic interaction was proposed to explain this behavior; in view of the fact that no dependence of the susceptibility on field strength was observed, such an interaction cannot be present.