The europium salts were prepared as follows: A mixture of 100 ml water containing 0·01 mole NaOH and an excess of the solid (water-insoluble) fluorenone acid was stirred until no more of the solid dissolved. The excess solid was removed by filtration and 3·3 × 10^{-3} moles of $EuCl_3$ (as a standardized 0·5 M aqueous solution) was added dropwise to the stirred filtrate over a period of 15 min. After an additional 2 hr of standing at room temperature, the yellow precipitate was filtered off, washed with water, and dried in a vacuum desiccator. No suitable solvent was found for recrystallizing these compounds. Elemental compositions are given in Table 1.

Aqueous solutions containing mixtures of NaEuEDTA and sodium fluorenone carboxylates were prepared as previously described for the benzoylbenzoates.(5) The sodium fluorenone carboxylates were prepared directly in solution by neutralizing the acid with NaOH.

Spectroscopy. Absorption spectra were determined with a Cary Model 14 spectrophotometer. Fluorescence spectra were obtained with a 1-m Jarrell Ash spectrometer. A photomultiplier with an S-20 characteristic response was used to detect the signal at the exit plane.

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J. inorg. nucl. Chem., 1966, Vol. 28, pp. 2765 to 2767. Pergamon Press Ltd. Printed in Northern Ireland

Perchlorate co-ordination in nickel (II) complexes with substituted anilines

(*Received* 1 *June* 1966)

Co-ordinated perchlorate with nickel (II) has recently been reported in the case of some complexes with either nitrogen or oxygen donor atoms.(1–7) As part of a study of the co-ordination chemistry of aromatic amines we have prepared some blue paramagnetic complexes of the type $[Ni(X\text{-}an)_4(ClO_4)_2]$ (X-an = aniline, 3-methylaniline, 3-chloroaniline, 4-methylaniline) containing co-ordinated perchlorate and the blue paramagnetic complex $[Ni(3\text{-methylaniline})_6](ClO_4)_2$ containing ionic perchlorate.

The complexes were prepared by leaving a mixture of hydrated nickel (II) perchlorate and 2,2-dimethoxypropane overnight and then adding a solution of amine in benzene. The mixture was concentrated to half volume and an equal volume of *i*-propanol added. The resulting complexes were filtered off, washed with ether and dried *in vacuo*. Analyses for the compounds are given in Table 1.

Table 1.—Analytical data for the complexes

	Calculated (%)				Found (%)			
Complex	Ni	C	H	N	Ni	C	H	N
$Ni(C_6H_5NH_2)_4(ClO_4)_2$	9·32	45·73	4·85	8·89	9·24	46·17	4·40	8·85
$Ni(3\text{-}CH_3C_6H_4NH_2)_4(ClO_4)_2$	8·56	49·00	5·29	8·16	8·54	49·24	5·25	8·21
$Ni(3\text{-}ClC_6H_4NH_2)_4(ClO_4)_2$	7·68	37·50	3·13	7·29	7·77	36·80	3·23	7·13
$Ni(4\text{-}CH_3C_6H_4NH_2)_4(ClO_4)_2$	8·56	49·00	5·29	8·16	8·56	49·09	5·43	8·39
$Ni(3\text{-}CH_3C_6H_4NH_2)_6(ClO_4)_2$	6·53	56·00	6·00	9·33	6·53	55·25	5·86	9·58

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The i.r. absorption bands (obtained in Nujol mulls) in the 1300–900 cm^{-1} region due to the perchlorate group are listed in Table 2. The complex [Ni(3-methylaniline)$_6$] $(ClO_4)_2$ exhibits i.r. bands characteristic of ionic perchlorate, with a broad, very strong absorption at 1070 cm^{-1} arising from the ν_3 antisymmetric stretching mode and a moderate absorption at 919 cm^{-1} due to the ν_1 symmetric stretching mode (i.r. inactive but present, due probably to lattice interactions). For unidentate perchlorate groups (C_{3v} symmetry) it has been shown that the ν_3 band of the free ion is split into two bands and the ν_1 mode becomes i.r. active.(1) This results in three strong bands at 1110–1165, 1010–1060 and 910–940 cm^{-1} due to the ν_4, ν_1 and ν_2 modes in C_{3v} symmetry.(1–7) In the tetrakis-complexes reported here strong i.r. bands are found at about 1130, 1020 and 910 cm^{-1}, indicating unidentate perchlorate groups.

TABLE 2.—I.R. BANDS OF THE PERCHLORATE GROUP IN THE COMPLEXES

Symmetry	T_d		C_{3v}		
	ν_3	ν_1	ν_4	ν_1	ν_2
	T_2	A	E	A_1	A_1
Band assignments†	asy. str.	sym. str.	asy. bend ClO(Ni)	sym. str. ClO_3	ClO(Ni) str.
$[Ni(3\text{-}CH_3C_6H_4NH_2)_6](ClO_4)_2$	1070 vs, b	919 m			
$Ni(C_6H_5NH_2)_4(ClO_4)_2$			1129 vs	1009 vs	900 s
$Ni(3\text{-}CH_3C_6H_4NH_2)_4(ClO_4)_2$			1124 vs	1021 vs	920 s
$Ni(3\text{-}ClC_6H_4NH_2)_4(ClO_4)_2$			1127 vs	1027 vs	913 s
$Ni(4\text{-}CH_3C_6H_4NH_2)_4(ClO_4)_2$			1126 vs	1019 vs	906 s

sym., symmetric; asy., antisymmetric; str., stretch; s, strong; m, medium; b, broad; v, very.
† Assignments are in accordance with earlier work.(1)

The diffuse reflectance spectrum (Table 3) of [Ni(3-methylaniline)$_6$]$(ClO_4)_2$ shows three bands I, II and III, typical(8) of octahedral high-spin nickel (II) and from these bands values of 9800 cm^{-1} for 10*Dq* and 975 cm^{-1} for B may be derived.(9) The spectra of the tetrakis-complexes, with a pronounced splitting of band I, indicate tetragonal structures with *trans*-co-ordinated perchlorate groups.(1–9) The magnetic moments (Table 3) of the complexes are all in the usual range for high-spin six-co-ordinate nickel (II).(10)

TABLE 3.—DIFFUSE REFLECTANCE SPECTRA AND MAGNETIC MOMENTS OF THE COMPLEXES

Complex	Absorption maxima (cm^{-1} × 10^{-3})					μ_{eff} Bohr magnetons
		I		II	III	
$[Ni(3\text{-}CH_3C_6H_4NH_2)_6](ClO_4)_2$		9·8		16·3	27·8	3·22
$Ni(C_6H_5NH_2)_4(ClO_4)_2$	8·5		11·3	15·9	28·8	3·21
$Ni(3\text{-}CH_3C_6H_4NH_2)_4(ClO_4)_2$	8·2		11·5	16·3	29·0	3·40
$Ni(3\text{-}ClC_6H_4NH_2)_4(ClO_4)_2$	8·6		11·0	15·9	28·2	3·28
$Ni(4\text{-}CH_3C_6H_4NH_2)_4(ClO_4)_2$	8·0		11·7	16·3	27·8	3·19

Other tetragonal complexes [Ni(X-aniline)$_4$$(ClO_4)_2$] (e.g. X = 3-bromo, 3-nitro, 4-bromo,3,4-dichloro) are being investigated. So far it has not been found possible to obtain any planar diamagnetic complexes of the type [Ni(X-aniline)$_4$]$(ClO_4)_2$, as have been found with the analogous

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compounds with substituted pyridines.(2,3,7) The results of further studies on these compounds will be published in due course.

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J. inorg. nucl. Chem., 1966, Vol. 28, pp. 2767 to 2768. Pergamon Press Ltd. Printed in Northern Ireland

Relationship between surface area of powdered UO_2 and its oxidation temperature

(*Received* 23 *May* 1966)

In applying the relationship derived by Imriš(1,2) between surface area S of powdered UO_2 and the difference in the final temperatures ΔT of oxidation of the two-step reaction $UO_2 \rightarrow U_3O_7 \rightarrow U_3O_8$ to a series of UO_2 specimens of different origin, we have found that the scatter of individual values of β (if $\beta = \Delta T/S$, as proposed by Imriš(1,2) for a certain value of S is not as little as to account for the experimental error of the determination only. Further, the course of log β on S seemed not to be linear but rather hyperbolic in the region of large surface areas (8–16 m^2/g).

For the verification of this assumption, a series of UO_2 specimens was prepared by reduction in H_2 at 700°C of UO_3 specimens calcined from ammonium polyuranate, uranyl nitrate, uranium peroxide, or hydrated UO_3(3) at temperatures between 200 and 450°, or by oxidation of UO_2 powders, pellets, or U metal(4) of different origin at temperatures between 400 and 650°C and subsequent reduction in H_2 at 700°C, in some cases with additional oxidation-reduction cycling as described by Seidl(4) and de Hollander.(5)

All these UO_2 specimens were heated in air on thermobalances described by Imriš(6) at the rate of temperature increase of 8°C/min. Final oxidation temperatures in both oxidation steps were determined by means of the method of the intersection of slopes.(1)

A plot of log β vs. log S (Fig. 1) showed that the dependence of ΔT on S can be more generally described by a straight line determined by means of the method of least squares:

$$\log \beta = k \cdot \log S + \log \psi \qquad (1)$$

where the values of k and log ψ are given in Table 1.

If the values of Imriš are substituted into this equation (specimens marked ● in Fig. 1), and if the rule of 3σ is applied, the relationship proposed by Imriš, which is a special case of Equation (1) lies within the range of maximum deviation of 3σ. It was, of course, obtained from observations carried out on two types of UO_2 only: (1) those prepared by direct reduction of ammonium polyuranate, and(2) those prepared by the reduction in H_2 of specimens of U_3O_8.(1,2)

For other individual types of UO_2 of a similar origin, described above, similar relationship with

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