

Reformulation of two Ni(II)-8-hydroxyquinoline Complexes from Calculated Structure Factors

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Abstract The compound that had been crystallographically identified as $\text{Na}[\text{NiQ}_2(\text{HQ})](\text{ClO}_4)$ (HQ = 8-hydroxyquinoline) contains no sodium, and instead is $[\text{H}_3\text{O}][\text{NiQ}_2(\text{HQ})](\text{ClO}_4)$. The lanthanum-nickel complex $[\text{YQ}(\text{HQ})_2][\text{NiQ}_3](\text{ClO}_4)$ that had been similarly identified contains no yttrium, and its formula is $[\text{H}_3\text{O}][\text{Ni}_2\text{Q}_3(\text{HQ})_3](\text{ClO}_4)_2$. The revision of the description of the crystal structures was effected by an examination of the bond dimensions that were derived by calculating the structure factors from the published atomic coordinates.

Keywords: Structure revision, Nickel(II) complex, Calculated structure factors

The reaction of nickel chloride, gadolinium perchlorate and 8-hydroxyquinoline in the presence of sodium *t*-butylacetate in water was reported to yield the six-coordinate compound, $\text{Na}[\text{NiQ}_2(\text{HQ})](\text{ClO}_4)$ (**1**), whose structure was determined by crystallography. The compound belongs to the monoclinic $P2_1/n$ space group [$a = 1.3546(7)$, $b = 1.2146(6)$, $c = 1.6421(7)$ nm, $\beta = 101.02(4)^\circ$], and there are four formula units in the unit cell^[1]. A similar reaction with yttrium perchlorate was claimed to afford the lanthanum-nickel complex $[\text{YQ}(\text{HQ})_2][\text{NiQ}_3](\text{ClO}_4)$ (**2**) [$P2_1/c$, $a = 1.6972(4)$, $b = 1.1128(3)$, $c = 2.2615(4)$ nm, $\beta = 103.16(2)^\circ$]^[2]. However, the published bond distances involving the yttrium atom could not be independently verified from the atomic coordinates, although, curiously, the corresponding bond angles could be easily derived from the table. The rare six-coordinate status of the yttrium atom as well as the fact that the bond distances (calculated from the atomic coordinates) are not significantly different from those involving the nickel atom cast doubts on the au-

thenticity of the structural determination. Indeed, if the yttrium(III) atom is replaced by a nickel(II) atom, the bond dimensions are normal, and the resulting formulation can also be reasonably expected of the synthesis; in the earlier reaction with gadolinium perchlorate, the lanthanum atom was not incorporated in the structure. These two crystal structures are re-interpreted and reformulated in this communication from the calculated structure factors for lack of original intensity data.

1 Calculations

The published table of atomic coordinates for (**1**) lists one sodium atom, one nickel atom, three quinolinolyl groups and one perchlorate group. The perchlorate group lies on the crystallographic two-fold axis; however, three oxygen atoms are bonded to the chlorine atom, two in general positions and one (O12) in a special position. Since the perchlorate ion has four oxygen atoms, atom O12 should be omitted from the table. More importantly, because the ion lies on a

two-fold axis, only two anions are present in the unit cell. A **SHELX** type of input file was then prepared that was checked by **PLATON**^[3] to ascertain the position of the other missing perchlorate group that would contribute two more perchlorate ions.

A **SHELX** type of input file was similarly prepared for (2). As the bond dimensions of the quinolinoly groups are unsatisfactory, the *hkl* - F^2 data were calculated^[4] for the $0 \sim 50^\circ 2\theta$ range; Mo- K_α radiation ($\lambda = 0.07107$ nm) was assumed in the calculations^[5], and all atoms were given a temperature factor of 0.0005 nm². The perchlorate group was excluded in the computations, and a nickel atom was used in place of the yttrium atom. The structure was refined on F^2 , and the quinolinyl groups were restrained into naphthalene groups by an **AFIX** 116 instruction. For the quinolinoly groups, the C - O and N...O interactions were restrained by **SADI** instructions in **SHELXL**-97^[6].

2 Discussion

The program **PLATON** found two symmetry-related voids of 0.172 nm³ in the unit cell of (1). Most probably, the perchlorate group is to be found at $(1/4, -0.152, 3/4)$. In the nickel bearing moiety, the O1 oxygen atom is 0.2345 nm from the O2 atom of a symmetry related moiety, so that these two atoms must be linked by a hydrogen bond; arising from this interaction, the molecule probably has only one neutral HQ entity. The sodium atom is linked to only two oxygen atoms (O3 and the symmetry-related O3*i* atoms) at 0.2935 nm. More likely, the sodium atom is an oxygen atom, and the ion would be the hydronium $[\text{H}_3\text{O}]^+$ cation that contributes one symmetry-independent hydrogen atom for bonding with the O3 oxygen atom, which bears a formal negative charge for the quinolinoly group that it belongs to. The second hydronium cation is most probably found at $(1/4, 0.582, 3/4)$. Balancing the charges leads to the conclusion that the nickellate would be the $\text{Na}[\text{Ni}_2(\text{HQ})]$ mono-cation. The correct structure of (1) is then $[\text{H}_3\text{O}][\text{Ni}_2(\text{HQ})](\text{ClO}_4)$. The calculated CHN elemental percentages for the revised formulation are in reasonably good agree-

ment with the reported values. Table 1 lists a partial list of the atomic coordinates of the revised structure. The quinolinyl group has been restrained to have idealized distances and angles; the structure of the mono-cation is shown in Fig. 1.

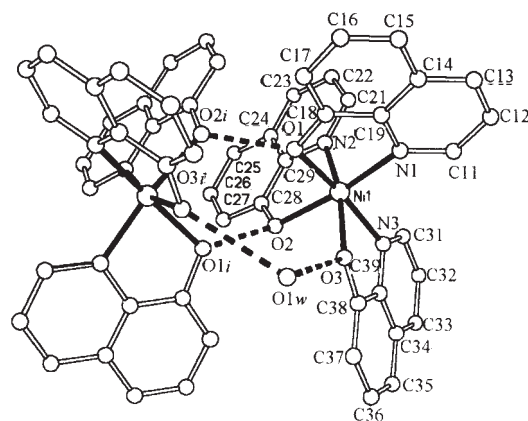


Fig. 1 Plot of the $[\text{H}_3\text{O}][\text{Ni}_2(\text{HQ})]$ cation of $[\text{H}_3\text{O}][\text{Ni}_2(\text{HQ})](\text{ClO}_4)$.

The hydronium ion is represented by the O1w atom. The dashed lines denote hydrogen bonds: O1...O2*i* = 0.2345 nm, O1w...O3 = O1w...O3*i* = 0.2953 nm. Symmetry code: $i = 1/2 - x, y, 1/2 - z$

The reported structure of (2) is marked by several chemical and crystallographic inconsistencies, but these could be reasonably explained if the yttrium atom is, in fact, a nickel atom. The second perchlorate group, omitted from the table of atomic coordinates, is most probably to be found at $(0.166, -0.0065, 0.204)$. The two nickellate octahedra are linked through their oxygen vertices by three hydrogen bonds, which suggests the existence of the dinuclear $[\text{Ni}_2\text{Q}_3(\text{HQ})_3]^+$ mono-cation. Because there are two perchlorate groups, one of which had been calculated by **PLATON**, the charges of the cations and ions would be balanced if a hydronium cation exists in the crystal structure. Unfortunately, the cell is too large for this to be located, although the program did reveal several solvent-accessible voids. On the basis of these voids, (2) is reformulated as $[\text{H}_3\text{O}][\text{Ni}_2\text{Q}_3(\text{HQ})_3](\text{ClO}_4)_2$. The bands in the infrared spectrum are also in agreement with the presence of water, although the authors had interpreted these^[2] in terms of

Table 1 Atomic coordinates for the $[\text{H}_3\text{O}][\text{Ni}_2(\text{HQ})]$ cation of $[\text{H}_3\text{O}][\text{Ni}_2(\text{HQ})](\text{ClO}_4)$ in $P2/n$ [$a = 1.3546(7)$, $b = 1.2146(6)$, $c = 1.6421(7)$ nm, $\beta = 101.02(4)^\circ$]

Atom	X	Y	Z	Atom	X	Y	Z
Ni1	0.2609	0.2514	0.0994	C22	0.1648	-0.0870	0.0260
O1	0.1485	0.2752	0.1666	C23	0.2293	-0.1443	0.0876
O2	0.3576	0.1975	0.2036	C24	0.2965	-0.0872	0.1474
O3	0.3157	0.4126	0.1343	C25	0.3609	-0.1444	0.2090
N1	0.1510	0.3039	0.0057	C26	0.4281	-0.0873	0.2688
N2	0.2347	0.0844	0.0840	C27	0.4308	0.0270	0.2670
N3	0.3816	0.2641	0.0389	C28	0.3664	0.0842	0.2054
O1w	1/4	0.5704	1/4	C29	0.2992	0.0271	0.1456
C11	0.1533	0.3174	-0.0779	C31	0.4132	0.1871	-0.0131
C12	0.0677	0.3524	-0.1325	C32	0.5080	0.1960	-0.0331
C13	-0.0202	0.3738	-0.1034	C33	0.5713	0.2820	-0.0009
C14	-0.0225	0.3602	-0.0197	C34	0.5398	0.3591	0.0511
C15	-0.1104	0.3816	0.0093	C35	0.6030	0.4451	0.0833
C16	-0.1127	0.3680	0.0930	C36	0.5715	0.5221	0.1355
C17	-0.0271	0.3331	0.1475	C37	0.4766	0.5132	0.1554
C18	0.0608	0.3117	0.1185	C38	0.4133	0.4272	0.1233
C19	0.0631	0.3253	0.0348	C39	0.4449	0.3501	0.0711
C21	0.1675	0.0273	0.0242				

the OH stretching of the neutral HQ groups.

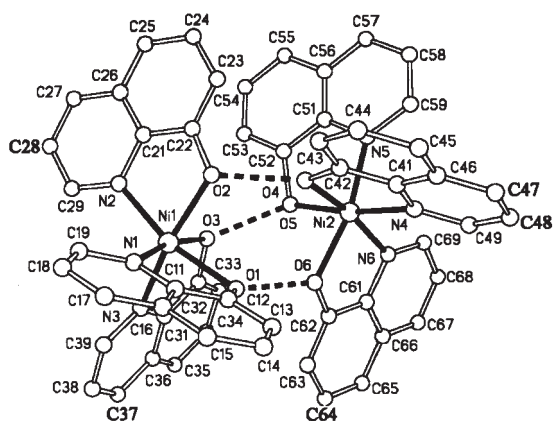


Fig. 2 Plot of the $[\text{Ni}_2\text{Q}_3(\text{HQ})_3]$ cation of $[\text{H}_3\text{O}][\text{Ni}_2\text{Q}_3(\text{HQ})_3](\text{ClO}_4)_2$.

The dashed lines denote hydrogen bonds: $\text{O1}\dots\text{O6} = 0.2212$ nm, $\text{O2}\dots\text{O4} = 0.2294$ nm, $\text{O3}\dots\text{O5} = 0.2381$ nm.

The reported distances and angles for the yttrium atom in (2) make little sense as the valence sum^[7] are too large; however, the valence sum is reasonable if the atom is calculated as nickel. Indeed, bond valence sums have been used for studying the coordination geometries of a number of transition metal complexes^[8]. The formulation of (2) is also supported by other crystallographically documented dinickel/quinolinol systems^[9-11].

In a crystallographic report, any bond dimension can be easily calculated from the cell constants, space group information and atomic coordinates, but this is possible only if the coordinates of all non-hydrogen atoms are published. The omission of the important atoms from the table could lead to an incorrect formulation.

Table 2 Atomic coordinates for the $[\text{Ni}_2\text{Q}_3(\text{HQ})_3]$ cation of $[\text{H}_3\text{O}][\text{Ni}_2\text{Q}_3(\text{HQ})_3](\text{ClO}_4)_2$ in $P2_1/c$
 $[a = 1.6972(4), b = 1.4128(3), c = 1.4128(3) \text{ nm}, \beta = 103.16(2)^\circ]$

Atom	X	Y	Z	Atom	X	Y	Z
Ni1	0.1717	0.2810	0.3477	C33	0.1129	0.4277	0.1721
Ni2	0.4068	0.3585	0.2805	C34	0.0520	0.4072	0.1212
O1	0.2446	0.1939	0.3032	C35	-0.0018	0.3338	0.1232
O2	0.2827	0.3244	0.4035	C36	0.0051	0.2809	0.1760
O3	0.1782	0.3892	0.2809	C37	-0.0487	0.2075	0.1780
O4	0.3976	0.3132	0.3667	C38	-0.0417	0.1547	0.2307
O5	0.3079	0.4419	0.2711	C39	0.0191	0.1752	0.2816
O6	0.3264	0.2522	0.2488	C41	0.5261	0.2450	0.3632
N1	0.1665	0.1578	0.3988	C42	0.4680	0.2630	0.3964
N2	0.1286	0.3840	0.3980	C43	0.4787	0.2289	0.4553
N3	0.0730	0.2486	0.2796	C44	0.5473	0.1767	0.4811
N4	0.5154	0.2791	0.3043	C45	0.6054	0.1587	0.4480
N5	0.4678	0.4791	0.3216	C46	0.5947	0.1928	0.3890
N6	0.4046	0.3838	0.1864	C47	0.6528	0.1748	0.3559
C11	0.2191	0.0905	0.3847	C48	0.6421	0.2089	0.2970
C12	0.2620	0.1098	0.3405	C49	0.5735	0.2611	0.2712
C13	0.3145	0.0425	0.3264	C51	0.4104	0.5427	0.3328
C14	0.3242	-0.0440	0.3564	C52	0.3285	0.5229	0.3126
C15	0.2813	-0.0633	0.4005	C53	0.2711	0.5865	0.3238
C16	0.2288	0.0039	0.4147	C54	0.2957	0.6698	0.3553
C17	0.1859	-0.0152	0.4589	C55	0.3776	0.6896	0.3755
C18	0.1333	0.0520	0.4730	C56	0.4350	0.6261	0.3643
C19	0.1237	0.1385	0.4430	C57	0.5170	0.6458	0.3845
C21	0.1922	0.4379	0.4309	C58	0.5743	0.5823	0.3733
C22	0.2716	0.4131	0.4314	C59	0.5498	0.4989	0.3418
C23	0.3352	0.4671	0.4643	C61	0.3453	0.3241	0.1537
C24	0.3194	0.5458	0.4965	C62	0.3029	0.2642	0.1841
C25	0.2400	0.5706	0.4960	C63	0.2436	0.2045	0.1514
C26	0.1764	0.5167	0.4631	C64	0.2267	0.2047	0.0883
C27	0.0970	0.5415	0.4626	C65	0.2691	0.2646	0.0579
C28	0.0334	0.4876	0.4297	C66	0.3284	0.3243	0.0906
C29	0.0492	0.4088	0.3975	C67	0.3708	0.3842	0.0602
C31	0.0660	0.3015	0.2268	C68	0.4301	0.4439	0.0929
C32	0.1199	0.3749	0.2248	C69	0.4470	0.4437	0.1560

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根据计算结构因子重新指定镍(II)8-羟基喹啉的两个络合物

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摘要 晶体学研究曾认为, 分子式是 $\text{Na}[\text{NiQ}_2(\text{HQ})](\text{ClO}_4)$ 的结构并不含有钠而应为 $[\text{H}_3\text{O}][\text{NiQ}_2(\text{HQ})](\text{ClO}_4)$. 相似地, 稀土-Ni 络合物 $[\text{YQ}(\text{HQ})_2][\text{NiQ}_3](\text{ClO}_4)$ 也不含有钇而应为 $[\text{H}_3\text{O}][\text{Ni}_2\text{Q}_3(\text{HQ})_3](\text{ClO}_4)$. 晶体结构描述的修正系根据文献报导的原子坐标计算结构因子所导出的结果.

关键词: 结构修正, 镍(II)络合物, 计算结构因子