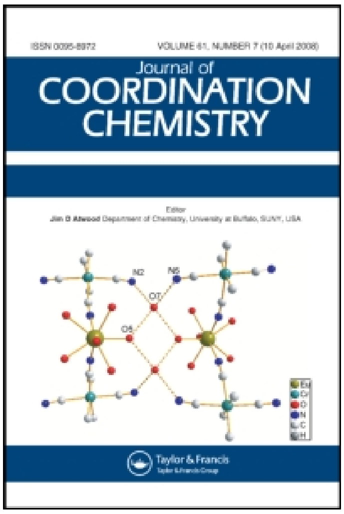

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THE INFRARED SPECTRA (4000 - 50 cm^{-1}) OF COMPLEXES OF QUINOLINE *N*-OXIDE AND ITS PERDEUTERATED ANALOGUE WITH METAL(II) PERCHLORATES OF THE FIRST TRANSITION SERIES

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THE INFRARED SPECTRA (4000 – 50 cm^{-1}) OF COMPLEXES OF QUINOLINE *N*-OXIDE AND ITS PERDEUTERATED ANALOGUE WITH METAL(II) PERCHLORATES OF THE FIRST TRANSITION SERIES

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Infrared assignments (4000 – 50 cm^{-1}) are presented for the complexes [M(quinO)$_n$](ClO$_4$)$_2$(quinO = quinoline *N*-oxide; n = 6 for Mn, Co, Ni; n = 5 for Zn, and n = 4 for Cu) and their perdeuterated analogues. The spectra are consistent with octahedral structures for the 6-coordinate complexes, a trigonal bipyramidal structure for the Zn(II) complex and a square planar structure for the Cu(II) complex, with some distortion from idealised symmetry evident for each complex. In the Mn(II) complex, strong coupling occurs between the νM-O of lowest frequency and the ligand vibration, αN-O (mode 45). In the Cu(II) complex, the single νCu-O is strongly coupled with the ring torsion (mode 28).

KEY WORDS: quinoline *N*-oxide, infrared spectra, complexes, isotopic labelling.

INTRODUCTION

As part of a series of investigations of the vibrational spectra of heterocyclic *N*-oxides and their metal complexes, we now report the infrared spectra of quinoline *N*-oxide (quinO) complexes derived from first transition series metal(II) perchlorates. Earlier vibrational studies have been confined to the studies of Ragsdale and his coworkers[1–3] of the infrared spectra (to 250 cm^{-1}) of the 6-coordinate species [M(quinO)$_6$](ClO$_4$)$_2$ (M = Mn, Co, Ni; Zn) and [Fe(quinO)$_6$](ClO$_4$)$_3$. These studies reported assignments for the N-O fundamentals based on those of Shindo,[4–6] which have subsequently been questioned.[7,8] The quinO complexes derived from Cu(II) perchlorate is reported for the first time. We were unable, after several attempts, to prepare the reported 6-coordinate Zn(II) complex. In our hands the synthesis always yielded the 5-coordinate species [Zn(quinO)$_5$] (ClO$_4$)$_2$. All attempts to prepare the Fe(II) complex failed; complete oxidation to the Fe(III) complex [Fe(quinO)$_6$](ClO$_4$)$_3$, always occurred.

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EXPERIMENTAL

The infrared spectra were recorded on a Perkin Elmer 983 spectrophotometer using Nujol (2000 to 200 cm^{-1}) and hexachlorobutadiene (4000 to 2000 and 1500 to 1200 cm^{-1}) mulls between CsI plates. Far-infrared spectra were recorded as Nujol mulls (500 to 50 cm^{-1}) between polyethylene plates on a Digilab FTS 16B/D interferometer.

The ligands were prepared as previously described.[8]

Preparation of $[M(quinO)_n](ClO_4)_2$ *(n = 6 for Mn, Co, Ni; n = 5 for Zn, and n = 4 for Cu)*

A solution of 0.1 g (0.27 mmole) metal(II) perchlorate (as the hydrated salt) in 5 cm^3 of dried absolute EtOH/dimethoxypropane (1:1 ratio) was allowed to stand for 20 minutes before being added, with stirring, to a similarly prepared solution of 0.35 g (1.91 mmole; 7:1 mole ratio) quinoline *N*-oxide dihydrate in 10 cm^3 of dried absolute EtOH/dimethoxypropane. The precipitate was collected by filtration, washed thoroughly with cold, dried absolute EtOH and with dried ether, and was dried over silica gel under reduced pressure. Yields of between 60 and 87% were obtained. Microanalytical data are given in Table 1.

The deuterated complexes were prepared as for their d_0 isotopomers, using one-half quantities of reactants. Yields of between 69 and 91% were obtained. Microanalytical data are given in Table 1.

RESULTS AND DISCUSSION

Quinoline *N*-oxide induces a weaker crystal field than pyridine *N*-oxide (pyO) (Table 2). Ragsdale and coworkers[1-3] examined the principal factors which affect the magnitude of 10*Dq*, *viz*, ligand basicity, steric effects and M → L and L → M π bonding. For the complexes represented in the present work, L → M π bonding will be weak or absent in view of the partial or complete occupation of the t_{2g} orbitals. As pointed

Table 1 Microanalyses of metal(II) complexes of quinoline *N*-oxide and their perdeuterated analogues.

		Experimental			Calculated		
	Colour	%C	%H	%H	%C	%H	%N
$[Mn(quinO)_6](ClO_4)_2 \cdot \frac{1}{2}H_2O$*	deep red	57.10	3.75	7.45	57.20	3.82	7.41
$[Co(quinO)_6](ClO_4)_2$	ochre	57.45	3.75	7.50	57.46	3.75	7.44
$[Ni(quinO)_6](ClO_4)_2 \cdot H_2O$	orange	56.60	3.80	7.30	56.57	3.85	7.33
$[Cu(quinO)_4](ClO_4)_2$	chocolate	51.00	3.35	6.60	51.29	3.35	6.64
$[Zn(quinO)_5](ClO_4)_2$	ivory	54.70	3.65	7.00	54.59	3.56	7.07
$[Mn(quin\text{-}d_7O)_6](ClO_4)_2 \cdot \frac{1}{2}H_2O$*	deep red	54.95	3.70	7.10	55.14	3.68	7.14
$[Co(quin\text{-}d_7O)_6](ClO_4)_2 \cdot H_2O$	ochre	54.45	3.60	7.00	54.45	3.73	7.07
$[Ni(quin\text{-}d_7O)_6](ClO_4)_2 \cdot 2H_2O$	orange	53.70	4.05	7.00	53.74	3.84	6.96
$[Cu(quin\text{-}d_7O)_4](ClO_4)_2$	chocolate	49.40	3.25	6.45	49.62	3.24	6.43
$[Zn(quin\text{-}d_7O)_5](ClO_4)_2 \cdot \frac{1}{2}H_2O$	ivory	52.10	3.25	6.95	52.25	3.51	6.77

*Light sensitive.

Table 2 Literature values of 10*Dq* for the Ni(II) complexes of some imines and their *N*-oxides.

	High Spin				Low Spin
ligand	quinO	pyO	bipyO$_2$	py	bipy
10*Dq*(cm^{-1})	7900	8400	8600	11 500	11 500
Reference	[1]	[9]	[9]	[9]	[9]

out by Nelson *et al.*,[1] the small difference in the basicities of quinO (pk_a 0.86) and pyO (pk_a 0.79) is scarcely sufficient to have a significant influence on the magnitude of 10*Dq*.[1] The steric effect of the bulkier quinO ligand may be expected to lead to a decrease in 10*Dq*, whereas an increase is observed relative to pyO. It was suggested[2,3] that the steric effect (if significant) was overruled by the superior π acceptor capacity of quinO. However, the evidence cited[1] for the latter effect (*viz*, the absence of a shift of the N-O stretch to lower frequencies on complexation) must be treated with caution in view of our conclusion[8] that the N-O stretch is a highly-coupled mode. Nevertheless, the greater contribution of orbital angular momentum to the magntic moments of the quinO complexes[1] indicates a shift of the π^* orbitals to lower energy (relative to pyO).[1] This would favour M → L π-interaction and support the conclusions of Nelson *et al.*[1] A literature search revealed only one crystal structure of a quinO complex: The adduct (p-tolyl)$_3$SnBr·quinO.[10] This exhibits an Sn-O-N angle of some 119°, with a near orthogonality (87°) of the Sn-O-N plane with that of the quinoline rings. Under these circumstances the geometry of complexed quinO is unsuitable for any significant M → L π bonding,[11] and it would not induce a large increase in 10*Dq*. We conclude, therefore, that the similarity in magnitude of 10*Dq* for the complexes of pyO and quinO results from the cumulative moderate effects (in quinO) of greater basicity and increased M → L π bonding, which is offset by the steric effect.

Unlike our previous studies of metal complexes in this series,[12,13] in the present study with quinO the complexes are not isostructural. The Mn(II), Co(II) and Ni(II) complexes have a coordination number of six. These complexes are likely to be octahedral with a localized symmetry of S_6 for the M(ON)$_6$ unit, similar to their pyO analogues.[14–17]

With a coordination of five, the molecule may adopt either a trigonal bipyramidal or a square pyramidal structure. In practice, a highly distorted intermediate of these often results. On the basis of ligand repulsions alone (whether considered as purely electrostatic or as Pauli repulsions from the bonding pairs) trigonal bipyramidal symmetry is favoured, being slightly more stable than square pyramidal.[18] However, the difference in stability between the two is so slight that crystal field effects and/or the presence of π bonding can favour square pyramidal geometry. Zn(II), being a d^{10} ion, has no crystal field stabilisation energy (CFSE), while the geometry of the ligand restricts the occurrence of significant π bonding. Hence the most likely structure for [Zn(quinO)$_5$](ClO$_4$)$_2$ is trigonal bipyramidal.

In four-coordinate complexes the tetrahedral conformation is generally considered to be favoured by steric requirements in terms of either simple electrostatic repulsions of charged ligands or van der Waal's repulsions of large ones. Square planar complexes are sterically less favoured, being prohibitively crowded by large ligands, and it is generally accepted that a prerequisite for their stability is the presence of nonbulky, strong field ligands which are sufficiently good π binders (to make up the energy "lost" through 4- rather than 6-coordination).[18] However, according to Karayannis *et al.*,[19,20] the presence of the pyridine ring (particularly when 2, 6-disubstituted) is effective in stabilising the square planar structure in four coordinate complexes with various pyridine *N*-oxides. Magnetic susceptibilities show four coordinate square planar structure for [M(II) (2, 6-dimethypyridine *N*-oxide)$_4$] perchlorates (M = Fe to Zn), rather than tetrahedral bridged structures.[19,20] Indeed, [Cu(pyO)$_4$](ClO$_4$)$_2$ has been crystallographically shown to be square planar.[21] The structure of the Cu(II) complex is therefore most likely to be square planar.

The full infrared assignments for M(II) (ClO$_4$)$_2$ complexes with quinO and its d_7 analogue are based upon the free ligands,[8] and are presented in Tables 3 and 4. The far-infrared spectra (625 to 50 cm^{-1}), reflecting the deuteration shifts of these complexes, are given in Table 5.

Table 3 Infrared assignments (4000 – 350 cm^{-1}) for metal(II) complexes of quinoline *N*-oxide.

Mn	Co	Ni	Cu	Zn	Assignment
3553 vwbr		3526 wbr			νO-H(H$_2$O)
3156 vw	3152 w	3155 w	3160 w	3158 w	comb
3100 mssh	3104 wm	3104 m	3110 s	3108 m	41(νC-H)
3077 s	3073 m	3076 s	3085 m	3079 m	1, 14 and 42(νC-H)
3021 m	3021 m	3020 mw	3027 w	3025 mw	2 and 15(νC-H)
			3020 wsh		30(νC-H)
2969 wm	2966 w	2970 w	2964 w		comb
	2928 w	2930 vw	2929 w	2928 w	
2949 w	2854 w	2853 w	2849 w	2844 w	
	2781 w	2773 vwbr	2782 wbr	2792 wbr	
2716 w	2711 w	2713 w	2715 vvw	2709 w	
2629 w	2622 vw	2625 vw	2624 vw	2623 w	
2586 w	2582 vw	2580 vw	2586 vw	2582 w	
2530 vw	2525 vw	2500 vw	2500 vw		
2458 w	2456 w	2456 w	2460 w	2456 w	
2407 w	2404 wbr	2416 wbr	2414 wbr	2402 w	
2366 vw	2359 vw	2373 w	2355 vw	2350 vw	
2326 w	2319 vw	2324 w	2321 w	2324 w	
2284 w	2291 vw	2284 w	2292 vvw		
2262 vw	2264 w		2265 w	2263 w	
2191 w	2189 w	2193 w	2195 w	2194 w	
2112 w	2110 vw	2111 w	2107 vw	2111 w	
2015 w	1999 w	2003 w	2027 w	2010 w	
	1951 w	1954 w	1955 w	1952 w	
1844 w	1846 w	1844 w	1866 w	1868 w	
1816 w	1816 w	1817 w	1831 w	1835 w	
1762 w		1762 vw	1772 w	1750 w	
	1712 w	1713 w	1717 w		
1685 w			1673 w	1677 vw	
1642 vwsh	1644 w	1642 vw	1638 w	1632 wsh	16(νring)
1620 wm	1620 wm	1621 wm	1618 wm	1619 m	31(νring)
1601 w	1603 w		1601 w	1602 w	comb
1587 w	1587 msh	1586 m	1588 m	1588 msh	comb
1576 s	1577 s	1578 s	1582 s	1581 s	4 (νring/νN-O)
1537 w	1527 w		1528 w		comb
1514 ms	1515 s	1516 s	1516 s	1515 s	44 (νring)
1501 w	1502 wsh			1491 w	comb
1456 ms	1456 s	1455 s	1457 m	1456 ms	8 (νring)

Table 3 *Continued*

Mn	Co	Ni	Cu	Zn	Assignment
1444 wsh	1445 msh	1445 msh	1447 m	1447 m	17 (νring/νN-O)
1398 vs	1398 vs	1398 vs	1397 vs	1395 vs	3 (νring)
1377 s	1374 s	1375 s	1379 s	1375 s	32 (νring/νN-O)
1335 wm	1335 wm	1336 w		1344 w	comb
1317 m	1315 ms	1319 ms	1315 m	1315 m	43(νring/νN-O)
1309 m		1311 ms	1308 m		
1268 s	1266 s	1269 s	1280 wsh	1265 s	34 (αC-H)
1262 ssh		1262 s	1271 s		18 (αC-H)
1229 s	1228 s	1228 s	1229 s	1229 s	29 (νN-O/νring)
1213 vs	1211 vs	1211 vs	1217 vs	1214 vs	46 (αC-H)
1184 s	1184 s	1187 s	1176 s	1176 s	19(αC-H)
1178 ssh	1177 mssh	1179 ssh			
1148 s	1149 s	1151 ms	1153 s	1149 s	5 (αC-H)
1141 s	1139 s	1140 s	1146 s	1141 s	33 (αC-H)
1080 vsbr	1087 vsbr	1085 vsbr	1090 vsbr	1083 vsbr	$\nu(ClO_4)$
1055	1057 ssh	1054 s	1051 s	1057 s	7 (αC-H)
	1046 ssh			1048 ssh	
1016 wm	1016 wm	1016 sm	1017 wm	1016 wm	10 (γC-H)
989 w	991 w	991 w	995 w	989 w	37 (γC-H)
980 wm	979 wm	980 wm	977 w	974 w	26 (γC-H)
968 wsh	968 w	969 w	965 w	961 w	comb
948 wsh	957 w	957 w			comb
938 w	937 w	938 w	937 wm	937 wm	21 (νring/νN-O)
929 w	930 wsh	929 w	930 w	930 w	$\nu(ClO_4)$
913 w	913 w		910 w	910 w	comb
	908 w	908 w		903 w	comb
882 s	880 s	880 s	880 s	880 s	47 (νring/νN-O)
861 m	868 ms	868 ms	870 m	868 m	39 (γring)
816 s	816 s	817 ms		815 s	11 (γC-H)
805 s	803 vs	804 ssh	806 vs	797 vs	38 (γC-H)
799 vs	798 vs	799 vs	801 s		23 (γC-H)
778 s	774 vs	774 m	770 s	772 s	36 (νring/νN-O)
767 vs	762 s	764 s		767 s	
736 m	735 s	734 ms	737 m	735 mwsh	6 (νring/νN-O)
725 s	724 s	724 s	727 s	723 s	27 (γC-H)
621 s	622 s	622 s	622 s	622 s	$\delta(ClO_4)$ and 48 (νring/νN-O)
583 s	581 ms	583 s	590 s	582 ms	12 (γring)
567 s	567 s	569 s	571 s	566 s	9 (νring/νN-O)
561 ms					
522 s	550 s	550 s	550 ms	548 s	20 (νring/νN-O)
499 ms	497 s	498 s	507 ms	500 s	40 (γring)
483 m	488 ms	490 ms	479 mw	482 w	24(γring)
	483 ms	483 m			
476 vw	475 vw				comb
468 vw	468 vw	468 vw	466 vw		comb
464 vw	463 vw	463 vw		464 w	comb
422 wm	422 wm	420 wm	450 m	420 w	28 (γring)

S = strong, m = medium, w = weak, v = very, sh = shoulder, br = broad, comb = combination.

Table 4 Infrared assignments (4000 – 350 cm^{-1}) for metal(II) complexes of quinoline-d_7 *N*-oxide.

Mn	Co	Ni	Cu	Zn	Assignment
3440 wbr	3530 w	3380 wbr		3416 mbr	νO-H(H$_2$O)
3153 w	3155 vw	3152 w	3152 vw	3152 mbr	comb
	2973 wm	2960 vw	2958 w		
2925 w	2935 w	2923 w	2929 w	2923 wsh	
2854 w	2861 w	2857 vw	2854 w		
2781 w	2792 vw	2780 w		2778 wsh	
	2780 vw		2769 vw		
2680 vw	2680 vw		2684 vw		
	2614 vwbr	2613 w	2622 vw	2623 w	
2463 w	2465 vwbr	2460 w	2455 w	2462 w	
2378 w	2377 w	2380 vw	2378 w	2378 w	
2338 wsh	2330 wsh	2342 w	2337 w	2336 wsh	
2312 mw	2314 mw	2312 w	2317 wm	2316 m	1 (νC-D)
2296 wm	2296 wm		2300 wm	2296 wm	41 (νC-D)
2283 wm	2285wsh	2287 w			30 (νC-D)
2268 wm	2278 wsh	2277 w	2272 w	2276 wm	2 and 14 (νC-D)
		2218 w	2222 w	2216 vw	comb
	2145 vw		2159 vw	2163 vw	
2101 vw	2094 w	2096 w	2098 w	2098 w	
2023 w	2019 w	2018 w	2036 w	2023 w	
		2000 w	2004 w	2010 wsh	
1938 vw	1925 vw	1920 w	1935 w	1932 w	
1835 vw		1830 w	1830 w		
	1818 vw		1815 vw		
1715 w	1712 w		1720 w	1708 wm	
1665 vw			1667 vw	1669 wmbr	δO-H(H$_2$O)
1631 w	1640 w	1645 vw	1645 w	1645 wbr	
	1620 w	1621 w	1621 w		comb
1598 m	1599 m	1599 ms	1599 ms	1597 ms	16 (νring/νN-O)
	1576 w	1571 w	1582 w		31(νring)
1557 w	1556 w	1558 w	1562 w	1565 w	comb
1536 s	1537 s	1537 s	1541 s	1538 s	4 (νring/νN-O)
1490 w	1490 w		1515 vw		comb
1456 s	1458 s	1459 s	1461 s	1458 s	44 (νring)
1437 wsh	1446 wm	1445 wmsh	1451 wmsh	1442 wm	comb
1424 vw	1427 vw	1429 vw	1428 vw	1425 vw	comb
1397 vw	1392 vw	1396 vw	1391 vw	1390 vwsh	comb
1378 ms	1380 ms	1380 ms	1380 m	1379 m	17 (νring/νN-O)
1361 s	1359 vs	1359 vs	1361 s	1359 s	3 (νring)
1314 s	1314 vs	1312 vs	1311 vs	1314 vs	43 (νring/νN-O)
1302 vs	1305 vs	1303 vs	1305 vs	1305 vs	8 (νring)
1242 s	1250 s	1248 s	1257 s 1251 s	1249 s	32 (νring/νN-O)
1213 w	1220 vw	1214 vw	1223 vw		comb
1204 w	1197 w	1204 w	1204 vwsh	1195 w	comb
1188 vw	1184 m	1189 vw	1194 w	1188 w	comb
1151 vs	1157 ssh 1147 vs	1160 ssh 1149 vs	1149 vs	1166 ssh 1148 vs	29 (νN-O/νring)
1080 vsbr	1092 vsbr	1087 vsbr	1109 vsbr	1089 vsbr	ν(ClO$_4$) and 46 (αC-D)
1028 s 1024 s	1027 ms	1028 s 1024 s	1026 s	1025 s	34 (αC-D)
1011 s	1012 s	1013 s	1012 vs	1012 s	19 (αC-D)
953 w	953 wm	953 w	955 vw	955 vw	comb

Table 4 *Continued*

Mn	Co	Ni	Cu	Zn	Assignment
930 w 928 w	931 w	931 w	930 w	932 w	$\nu(\mathrm{ClO_4})$ and 21 (νring/νN-O)
877 s	877 s	878 ssh 876 s	879 s	878 s	7 (αC-D) and 33 (αC-D)
	857 w	850 w			comb
842 wm	844 m	843 m	845 w	845 wm	37(γC-D)
828 m	830 m	838 wm	831 m	830 msh	5 (αC-D)
825 msh	827 m	827 wm	827 wmsh	827 m	10 (αC-D)
	814 wsh	812 w	813 w	811 w	18 (αC-D)
807 vw	806 w	806 w			comb
784 s	788 ssh 781 s	783 s	793 s 788 s	786 s	47 (νring/νN-O)
	770 wsh	768 w	773 wm	770 w	39 (γring)
760 s	759 w	764 w	756 vw	753 w	26 (γC-D)
744 ms	743 ms	743 m	746 m	744 m	36 (νring/νN-O)
721 m	720 w	722 w	727 w 722 w	722 w	6 (νring/νN-O)
680 s	679 s	682 s	684 s	683 s	38(γC-D)
666 w	668 vw	668 vw	672 vw		comb
650 wsh	651 w	651 wm	653 m	651 w	11 (γC-D)
639 ms	636 vs	629 vs	632 vs	633 vs	23 (γC-D)
623 vs	622 vs	622 vs	623 vs	624 vs	$\nu(\mathrm{ClO_4})$
594 m	600 m 596 msh	600 s	605 s	599 m	27 (γC-D)
564 ms	567 ms	563 s	572 s	567 s	48 (νring/νN-O)
	544 m	544 m	547 m	548 m	comb
539 ms 529 msh	536 ms	532 s	532 s	536 m 529 m	12 (γring)
497 s	494 s	496 s	508 s	500 s	9 (νring/νN-O)
487 ms	485 ms	489 s 485 ssh	592 ms	487 s	20 (νring/νN-O)
460 mw	464 m	471 w 463 w 455 w	455 mw	462 wsh 456 wm	40 (γring)
416 w 411 wm	412 m	419 wm 412 wm	412 m	411 wm	24 (γring)

The absence of perchlorate coordination in all complexes is evident from the infrared spectra (Table 3 to 5). The perchlorate ion with T_d symmetry is characterised by a very intense broad infrared band (with shoulders) at $1100\,\mathrm{cm}^{-1}$ (ν_3), a strong sharp band at $625\,\mathrm{cm}^{-1}$ (ν_4) and a weak (infrared forbidden) band at $930\,\mathrm{cm}^{-1}$.[22] The broadness and shoulders present in ν_3 may be ascribed to its being a triply degenerate F_2 vibration, to $\mathrm{ClO_4}$ being disordered, as well as to presence of the $^{37}\mathrm{Cl}$ isotope (24% natural relative abundance).

The local symmetry of the perchlorate ion is reduced to C_{3v} in monodentate

Table 5 Far infrared specta (625 – 50 cm^{-1}) of metal(II) perchlorate complexes with quinoline *N*-oxide and its perdeuterated analogue.

	quinO		Mn		Co		Ni		Cu		Zn		Assignment
	-d_0	-d_7	-d_0	-d_7	-d_0	-d_7	-d_0	-d_7	-d_0	-d_7	d_0	-d_7	
			621 s	(625 vs)	622 s	(622 vs)	622 s	(623 vs)	622 s	(623 vs)	622 s	(624 vs)	δ(ClO$_4$)
48	628	(564)		(564 ms)		(567 ms)		(563 s)		(563 s)		(567 s)	48 (νring/νN-O)
						(544 m)		(545 w)		(547 m)		(548 wm)	comb
12	610	(526)	528 s	(539 ms) (529 msh)	581 ms	(536 ms)	583 s	(532 s)	590 s	(532 s)	582 ms	(563 ms) (529 ms)	12 (γring)
9	557	(508)	567 s 561 ms	(497 s)	567 s	(494 s)	569 s	(496 s)	571 s	(508 s)	566 s	(500 s)	(νring/νN-O)
20	545	(497)	552 s	(487 ms)	550 s	(485 ms)	550 s	(489 s) (485 ssh)	550 ms	(492 ms)	548 s	(487 s)	20 (νring/νN-O)
40	480	(441)	499 ms	(460 mw)	497 s	(464 m)	498 s	(471 w) (463 w) (455 w)	507 ms	(455 mw)	500 s	(462 wsh) (456 wm)	40 (γring)
24	466	(416)	483 m	(416 w) (411 wm)	488 ms 483 msh	(412 m)	490 ms 483 m	(419wm) (412 wm)	479 mw	(412 m)	482 w	(411 wm)	24 (γring)
			476 vw		475 vw								comb
			468 vw		468 vw		468 vw		466 vw				comb
			463 vw		463 vw		463 vw				464 w		comb
28	422	(374)	422 wm	(378 wm) (370 wm)	422 wm	(371 wsh)	420 wm	(373 w)	450 m 397 ms	**(362 s)**	420 w	(379 w) (373 w)	28 (γring)
					366 s	**(352 s)**	**371 s**	**(350 s)**			**364 s**	**(349 s)**	
35	365	(340)	**349 s**	**(333 s)**		**(346 s)**	**358 s**	**(341 m)**					νM-O and 35 (νring)
			338 s	**(323 s)**	**354 s**	(329 wsh)	350 mssh	(330 msh)			**344 w**		
45	321	(307)	297 m	(275 m)	320 mw	(302 m)	322 m	(305 m)	321 m	(308 ms)	320 m	(304 wm)	45 (αN-O)
					300 w	(277 vw)	301 vw	(279 w)			300 wsh	(283 wsh)	comb
					280 vw		280 vw	(264 vvw)			285 vvw		comb
			227 m	(217 m)	238 w	(221 wsh)	243 wm	(229 wm)	262 wm	(248 wm)	239 w	(223 wm)	τMO/NO
											230 w	(217 wm)	τMO/NO
13	211	(196)	211 m	(199 m)	215 w	(210 m)	233 vwsh		217 vw		219 wm	(207 wm)	13 (γring)
					204 w		209 wm	(200 m)					τMO/NO
25	185	(170)	188 m	(174 ms)	189 m	(177 msh)	196 m	(186 wm)	194 w	(181 wmsh)	189 m	(174 wm)	25 (γring)
22	185	(175)	172 wm	(165 ms)	178 wsh	(169 m)	180 wsh	(172 wsh)	181 wm	(173 m)	166 m	(159 m)	22 (γN-O)
			134 vw	*(128 vvw)*	*135 vvw*	*(122 vvw)*	*140 vw*		*141 vwsh*	*(135 wsh)*	*145 vw*		δMON
			114 vvw	*(112 w)*					*127 w*	*(120 w)*	*129 w*	*(122 w)*	δMON or τMO/NO
			83 w	(81 w)	93 vwsh	(90 wsh)		(105 vw)	*99 w*	*(96 wm)*	*102 vw*	*(103 w)*	τMO/NO and δOMO
			75 w	(69 w)	74 w	(70 wm)	76 w	(75 w)			*75 w*	*(72 w)*	δOMO or τMO/NO
			64 w	*(55 wsh)*	*60 w*	*(59 wsh)*	*50 w*	*(50 w)*	*63 w*	*(60 w)*	*60 vwsh*		δOMO

Bold face = M-O stretch, italics = M-O bend. *N.B.* -d_7 band at 600 cm^{-1} (medium to strong) not included as it arises from -d_0 band (mode 27) above 630 cm^{-1} (see Tables 3 and 4).

perchlorate and to C_{2v} or C_s in bidentate perchlorate. Monodentate perchlorate is characterised by two very strong bands between 1200 and 1000 cm^{-1}, a strong band at 930 cm^{-1}, a strong band at 625 cm^{-1} (sometimes split) and a weak to medium band at 480 cm^{-1}.[18] Bidentate perchlorate is characterised by an additional strong band between 1270 and 1245 cm^{-1}, and by further splitting of the two bands at 625 and 480 cm^{-1}.[22]

As expected with the large size of the ligand quinO, resolution of the localized ligand symmetry into the molecular symmetry components is not complete. Even so, fourteen ligand fundamentals show band splitting on complexation, namely modes 47(-d_7), 43(-d_0), 40(-d_7), 36(d_0), 34(-d_7), 32(-d_7), 28(-d_7), 24, 20(-d_0), 12(-d_7), 9(-d_0), 7(-d_0), and 6(-d_7). Of these, only two are αC-H bends (modes 34 and 7), while the rest are ring modes (modes 40, 28, 24, and 12 are γring modes, the others being νring modes coupled with νN-O).[8] With band-splitting being experienced by only two αC-H bends (out of the 14 αC-H modes expected for both isotopomers), such splitting may be a result of the particular energy of these two vibrations. Thus, the frequency of mode 34(-d_7) (found at 1055 cm^{-1} in the free ligand) is similar to that of mode 7(-d_0) (found at 1054 cm^{-1} in the free ligand).[8]

While only the trigonal bipyramidal Zn(II) complex is expected to yield a significant perturbation of the localized ligand symmetry (with its different axial and equatorial ligand environment), the splitting of the ligand bands occurs in the spectra of the complexes of other metals also. This splitting may simply indicate a better resolution of the localized ligand symmetry into the molecular symmetry components. However, the number of fundamentals showing splitting on complexation is (with the exception of the Cu(II) complexes experiencing Jahn-Teller perturbation of the localised symmetry of the ligand) larger than that found for the three previous series of complexes investigated.[12,13] Therefore, splitting of the ligand bands in this series of complexes may be indicative of some distortion of the octahedral and square planar structures, resulting from greater perturbation of the localized ligand symmetry within these complexes. Future crystal structure determinations of the ML_6 and ML_4 complexes with quinO would therefore be of some interest.

The assignment of the M-O fundamentals (Table 5), particularly the M-O stretches, is complicated by the presence[8] of five low-lying internal ligand fundamentals below 450 cm^{-1}. The assignment of the ligand wagging vibrations (δMON, τNO, τMO) are based upon those of pyO.[14-16] The two bands in the regions *ca* 300 cm^{-1} and *ca* 285 cm^{-1} have been assigned as combination or difference bands since they lie above the expected region for the highest τMO/τNO region.[14-16] Considering the greater mass of quinO, it is unlikely that these ligand wags are to be found at higher frequencies than their pyO analogues.

Of the six νM-O, six δMON, six τNO, six τMO and nine δOMO vibrations associated with the $M(ON)_6$ unit (for S_6) symmetry four δOMO ($2A_u$ and $2E_u$) and two each of νM-O, δMON, τNO and τMO (each set with the representation of A_u and E_u) are infrared active.

For Mn(II), Co(II) and Ni(II) the expected two M-O stretches and five of the six ligand wagging modes (δMON, τNO and τMO) are observed. Of the four δOMO bands expected, two are undoubtedly to be found below 50 cm^{-1} (the limit of this work) as was the case for their pyO analogues.[14-16] The band at *ca* 60 cm^{-1} (d_0) is assigned to δOMO. The same assignment given to the band at *ca* 75 cm^{-1} (d_0) is only tentative, since the greater mass of quinO may result in lower δOMO bends compared with pyO. As an alternative assignment, this band may be the sixth ligand wag. Studies below $50\,cm^{-1}$, or a normal coordinate analysis, would provide a more conclusive assignment.

The difficulty in assigning M-O vibrations because of the presence of internal ligand modes is clearly demonstrated in this work by the coupling experienced in the Mn(II) complex between the planar bend, αN-O (mode 45) and the lowest νM-O. Mode 45 for the Mn(II) complex is found some 20 to $25\,cm^{-1}$ lower in frequency than in the other complexes, and also below that of the free ligand ($-d_0$) (Table 5). It is suggested that this abnormally low frequency is a result of coupling between mode 45 (expected at $320\,cm^{-1}$ for quinO-d_0) and the νM-O of lowest frequency (expected at *ca* $325\,cm^{-1}$). This leads to a (higher) coupled νM-O at $338\,cm^{-1}$ and a (lower) coupled αN-O at $297\,cm^{-1}$. This suggestion is supported by the fact that while the lowest νM-O of the 5-coordinate Zn(II) complex is at a stimilar frequency to that of the 6-coordinate Mn(II) complex, the αN-O of the Zn(II) complex is at the expected frequency of $320\,cm^{-1}$ ($-d_0$). Furthermore, νM-O for $[Mn(pyO)_6](ClO_4)_2$ is found at $312\,cm^{-1}$ [17] and, therefore, a frequency of *ca* $325\,cm^{-1}$ is expected for the quinO analogue. The conclusion is that the νM-O of lowest frequency for the Mn(II) complex is not a pure vibration. It is noted that this coupling is maintained on deuteration.

A further illustration of the difficulty in assigning the M-O vibrations (which results from the presence of ligand bands) is seen in the masking of the ring mode (mode 35) by the strong M-O stretches in the d_0 complexes. This mode is also observed only as a weak shoulder in the deuterated complexes of Co(II) and Ni(II).

Four-coordination, theoretically, gives rise to four each of νM-O, δMON, τNO and τMO and to five δOMO vibrations. For tetrahedral coordination with T_d symmetry (viewing the MO_4 unit) one νM-O (F_2) and one δOMO (F_2) are infrared active. Alternatively for a $M(ON)_4$ unit with C_{2v} symmetry, four infrared active νM-O ($2A_1$, B_1 and B_2) and four δOMO ($2A_1$, B_1, B_2) are expected, while the twelve wagging modes of the ligands yield ten infrared active vibrations ($4A_1$, $3B_1$ and $3B_2$).

For square planar symmetry, the most likely conformation is that described by Lee *et al.* as the *swastika*.[21] That is, D_{4h} symmetry for the MO_4 unit yielding one infrared active νM-O (E_u) and two δOMO (A_{2u} and E_u), or C_{4h} symmetry for the $M(ON)_4$ unit, for which one infrared active νM-O (E_u) and two δOMO (A_u and E_u) are likewise expected and for which four infrared ligand wagging modes (A_u, B_u and $2E_u$) are expected.

From Table V, the presence of one νM-O, two δOMO and three of the ligand wagging vibrations for the Cu(II) complex fully supports the existence of square planar coordination. The higher frequencies of νM-O and δOMO, compared with the 6-coordinate complexes, is expected to result from a decrease in the coordination number.[17] However, when compared with νM-O for $[Cu(pyO)_4](ClO_4)_2$ (at $422\,cm^{-1}$),[17] the M-O stretch for Cu(II) complex with quinO is very low, while the frequency of $450\,cm^{-1}$ for the ring torsion (mode 28) is abnormally high. This indicates probable coupling between these two vibrations (which is feasible since both are expected at *ca* $420-430\,cm^{-1}$). This coupling differs from that experienced by the Mn(II) coupling in that there appears to be deuteration-decoupling of the two vibrations, with the strong νM-O masking the ligand band in the perdeuterated complex.

Five νM-O, seven δOMO and fifteen ligand wagging modes (five each of δMON, τNO and τMO) are associated with the five-coordinate $M(ON)_5$ unit. The trigonal bipyramidal conformation has C_1 symmetry in which all the vibrations are expected to be infrared active. The simpler MO_5 unit with D_{3h} symmetry would yield two infrared active stretches (A_2'' and E') and three δOMO bends (A'' and $2E'$). The alternative square based pyramidal structure has C_{4v} symmetry for the MO_5 unit, giving rise to three infrared active νM-O ($2A_1$ and E) and three δOMO (A_1 and $2E$). This symmetry is similarly lowered to C_1 in considering the $M(ON)_5$ unit.

The presence of only two νM-O (at 364 cm^{-1} and 334 cm^{-1}) and three δOMO bands in the infrared spectrum of the Zn(II)-d_0 complex supports a trigonal bipyramidal structure. The high frequency of νM-O in the Zn(II) complex is accounted for by its lower coordination number.[17] The νM-O band of highest frequency in the spectrum of the Zn(II) complex is of the order of that found in the Co(II) complex. That this is indicative of penta-coordination, and that it does not fit the Irving-Williams series,[23] is demonstrated by a naïve calculation from which the expected increase in frequency of νM-O resulting from the loss of one ligand may be determined. From the infrared data of M(II) complexes with pyO,[17] the predicted M-O stretching frequency for the 5-coordinate $Zn(pyO)_5$ cation [$\nu Zn_{(5)}$] may be roughly calculated from

$$\nu Zn_{(5)} = \left(\frac{\nu Cu_{(4)}/\nu Cu_{(6)} - 1}{2} + 1\right) \cdot \nu Zn_{(6)}$$

as 369 cm^{-1}. This is similar to the observed νM-O frequency of $[Zn(quinO)_5](ClO_4)_2$ and therefore supports the latter assignment. The three bands at 102 cm^{-1} (-d_0), 75 cm^{-1} (-d_0) and 60 cm^{-1} (-d_0) are tentatively assigned to δOMO. The fact that their frequencies are higher than those of the Mn(II), Co(II) and Ni(II) complexes may be ascribed to the lower coordination number of the Zn(II) complex.

In conclusion, the full infrared assignment of M(II) complexes with quinO and its fully deuterated analogue reveals the formation of hexa-, penta- and tetra-coordinate complexes having distorted octahedral, trigonal bipyramidal and square planar conformations, respectively. It is noteworthy that the metal-oxygen stretches of the Mn(II) and Cu(II) complexes are strongly coupled with internal ligand vibrations, the nature and extent of the coupling being determined by the coordination number of the complex.

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