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Lophine Complex with Nickel(II) Perchlorate

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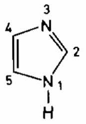
Numerous metal complexes with C-substituted imidazoles have been reported [1–8]. The presence of substituents at the 2-ring position of imidazole (*1*) introduces steric hindrance influencing both of the potential binding N-sites, while substitution at the 4- or 5-ring position will primarily affect the N(3) or N(1) nitrogen site, respectively. Steric effects in substituted imidazoles may influence in a variety of ways the nature of the metal complexes that can be synthesized with each particular imidazole ligand. For instance, significant steric hindrance, especially when arising from substituents at the C(2) carbon, will lower the highest possible ligand to metal ratios in solvates of imidazole derivatives with divalent metal perchlorates. In fact, whereas imidazole and N(1)-substituted imidazoles form 6:1 cationic complexes with Co^{2+} and Ni^{2+} (*i.e.*, $[M(LH)_6]^{2+}$) [2, 9], the corresponding complexes with 2-phenylimidazole are of the $[M(LH)_4]^{2+}$ type [2]. Another effect is the increased stability to oxidation of Cu^I complexes with imidazoles, with increasing steric hindrance near the binding site [1]. It was of interest to us to explore the possibility of isolating well-defined 3d metal complexes with a severely sterically hindered imidazole ligand, bearing bulky substituents in all three of the ring carbon atoms. Accordingly, we elected to investigate lophine (lopH; *2*, 2,4,5-triphenylimidazole) and initiated synthetic work in this direction. The present communication deals with the preparation and characterization of a complex of this ligand with Ni^{II} perchlorate. Previous studies with lopH had shown that $AlCl_3$ and $ScCl_3$ adducts of this ligand, involving low ligand to metal ratios, can be prepared [7, 8]. Moreover, quite recently lopH chemiluminescence was shown to be enhanced by ultratrace amounts of Co^{II} [10] or Cr^{VI} [11], and methods for the analytical determination of these species by lopH chemiluminescence have been developed [10, 11].



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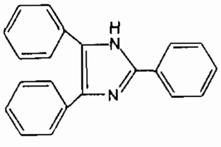

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The synthesis of the new complex was made by procedures similar to those employed for the isolation of adenine complexes with 3d metal perchlorates [12], *viz.*: A solution of 1 mmol of hydrated $Ni(ClO_4)_2$ in ethanol–triethyl orthoformate (1:1 v/v) was warmed for 2 h at 40–50 °C, then 0.5 mmol lopH were added, and the resultant mixture was refluxed overnight. A light green solid complex, analyzing as $Ni_2(lop)(ClO_4)_3 \cdot 10H_2O$ (analysis, found (calcd.)%: C 28.0(28.3); H 3.8(4.0); N 3.0(3.1); Ni 12.8(13.2); Cl 12.15(11.9)) was obtained in 50% of the theoretical yield. The complex was separated by filtration, washed with ethanol–triethyl orthoformate, and stored *in vacuo* over P_4O_{10}. Attempts at preparing other $Ni(ClO_4)_2$ complexes with lophine, involving higher ligand to Ni^{II} ratios, were also made by employing the same synthetic procedure, but using 1–3 mmol lopH/mmol $Ni(ClO_4)_2$. In all these cases, solids consisting of mixtures of a Ni^{II} complex with lophine and uncomplexed lopH were isolated. Similar phenomena were reported by Guichelaar and Reedijk in their attempts to synthesize adenine and i-methyladenine complexes with 3d metal salts, involving high ligand to metal ratios [13].

The new Ni^{II} complex is insoluble in organic media. Characterization studies show that it is a magnetically normal high-spin hexacoordinated Ni^{II} species (μ_{eff} at 299 K = 3.03 μ_B), and has an approximate Dq of 932 cm^{-1} (solid-state (Nujol mull) electronic spectrum, nm: $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ 417; $\rightarrow {}^3T_{1g}(F)$ 662, 718; $\rightarrow {}^3T_{2g}(F)$ 1073), which is consistent with occupation of the first coordination sphere of each Ni^{2+} ion by five aqua and one imidazole nitrogen ligands; in fact, Dq for $[Ni(OH_2)_6]^{2+}$ is 885 cm^{-1} [14], while the corresponding $[NiL_6]^{2+}$ cationic complexes with imidazole and substituted imidazoles show Dq values of 1050–1100 cm^{-1} [9]. The i.r. spectrum of the complex shows the ν(OH) and δ(HOH) vibrational modes of coordinated water at 3380(s,b) and 1633(m,sh) cm^{-1} [15]. The i.r. bands of free lopH at 1600–1450 cm^{-1}

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(1601m, 1587m, 1565w, 1537w, 1503s, 1488s) [16] undergo small shifts and occasional splittings upon Ni^{II} complex formation, occurring at 1611(m), 1592(m), 1555(w,b), 1512(s), 1500(s), 1473(s) cm^{-1}. The ν(NH) absorptions of free lopH at 2800–2500 cm^{-1} [16] are absent from the spectrum of the new complex, as would be expected [12], since the ligand is in the monodeprotonated anionic form (lop^-). The perchlorate groups are exclusively ionic, as demonstrated by the single character of the ν_3 and $\nu_4(ClO_4)$ fundamentals, which appear at 1090(vs,b) and 622(s,sharp) cm^{-1} [17]. Tentative Ni–ligand band assignments, compatible with a hexacoordinated NiO_5N species [4, 9, 15, 18], are as follows, cm^{-1}: ν(Ni–O) (aqua) 395ms; ν(Ni–N) 252m, 229sh.

In conclusion, it appears that lopH is too bulky a ligand to yield complexes involving high ligand to metal ratios; even a 1:1 complex could not be isolated, at least under our synthetic conditions. However, the steric hindrance introduced by the three phenyl substituents of the ligand is not severe enough as to make the two imidazole nitrogens unavailable for coordination, and a 1:2 complex of lop^- with Ni^{II} was indeed isolated. The evidence presented favours a dimeric structure of the $[(H_2O)_5Ni-lop-Ni(OH_2)_5](ClO_4)_3$ type, involving a binuclear complex cation with five terminal aqua ligands per Ni^{II} ion and a bridging anionic lop^- ligand, coordinating through its two imidazole nitrogens to the adjacent Ni^{2+} ions. This type of bridging is common not only in bi- or poly-nuclear complexes with anionic imidazole ligands [19], but also in linear chain-like polymeric complexes with neutral imidazole derivatives, in which the labile proton is not located at an imidazole nitrogen, as, for instance, 1H-purine [20]. The normal ambient temperature magnetic moment of the new complex was not unexpected. In fact, bi- or poly-nuclear Ni^{II} compounds with single bridges of diazole or diazine ligands exhibit normal magnetic behaviour at room temperature, showing evidence of antiferromagnetic exchange interactions only at lower temperatures (below 120 K) [21].

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