Syntheses, Structures and Vibrational Spectroscopy Studies of Copper(I) Perchlorate : Benzonitrile Adducts (1 : *n*) of *n* = 2, 3, 4, 5 Stoichiometry

Graham A. Bowmaker[a], Dip Singh Gill[b,c], Brian W. Skelton[b], Neil Somers[b], and Allan H. White[b]

[a] Department of Chemistry, University of Auckland, Private Bag 92019, Auckland, New Zealand
[b] Chemistry M313, University of Western Australia, Crawley, W.A. 6009, Australia
[c] Department of Chemistry, The Panjab University, Chandigarh, India 160014

Reprint requests to Prof. A.H. White. E-mail: ahw@crystal.uwa.au

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Dedicated to Professor Hubert Schmidbaur on the occasion of his 70th birthday

Syntheses and room-temperature single crystal X-ray structure determinations are recorded for an array of complexes formed between copper(I) perchlorate and benzonitrile of $CuClO_4$: PhCN (1:*n*) stoichiometry. Copper(I) perchlorate crystallized from neat benzonitrile solution yields a 1:5 $CuClO_4$: PhCN adduct, shown by the X-ray study to be of the form $[Cu(NCPh)_4](ClO_4)$. PhCN, and, on recrystallization from dichloromethane, the 1:4 adduct, shown to be $[Cu(NCPh)_4](ClO_4)$, the copper(I) atom in both the $n = 4, 5$ adducts being in a quasi-tetrahedral four-coordinate environment, $< Cu - N > 1.99$ Å. Heating of either of the above materials under vacuum to $70 - 80^{\circ}$ or $85 - 90$ °C (*Care*!) yields 1:3 and 1:2 adducts respectively which may be crystallized from dichloromethane. The 1:3 adduct is shown to be of the form $[(PhCN)_3Cu(O\!ClO_3)]$, the CuN_3 array quasi-trigonal planar (ΣN-Cu-N 358.$_0$°; Cu-N 1.906(4)-1.958(4), <> 1.93 Å), with a long unidentate perchlorate oxygen approach (Cu…O 2.404(4) Å). The 1:2 adduct comprises a pair of quasi-linear [(PhCN)Cu(NCPh)] moieties (Cu-N 1.884(6), 1.866(5) Å; N-Cu-N 158.6(3)°] linked about an inversion centre by a pair of oxygen atoms from centrosymmetrically related perchlorate groups, so that a weakly bound four-membered $Cu(\mu\text{-}O)_2Cu$ central ring is obtained (Cu…O 2.445(4), 2.502(6) Å). The structural data provide a basis for a comprehensive vibrational spectroscopic study across the whole array. These spectra show features that can be attributed to the structural changes that are observed with the change in the number of benzonitrile molecules in the compounds. The vibrational spectra of the acetonitrile complex $[Cu(NCMe)_4](ClO_4)$ have also been recorded and used to assist in the assignment of the spectra of the various stoichiometries of the benzonitrile compounds.

Key words: Copper Perchlorate, Benzonitrile, Structure, Infrared Spectroscopy, Raman Spectroscopy