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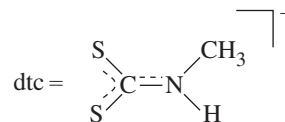
## General References

The official documents on IUPAC nomenclature are G. J. Leigh, editor, *Nomenclature of Inorganic Chemistry*, Blackwell Scientific Publications, Oxford, England, 1990 and J. A. McCleverty and N. G. Connelly, editors, *IUPAC, Nomenclature of Inorganic Chemistry II: Recommendations 2000*, Royal Society of Chemistry, Cambridge, UK, 2001. The best single reference for isomers and geometric structures is G. Wilkinson, R. D. Gillard, and J. A. McCleverty, editors, *Comprehensive Coordination Chemistry*, Pergamon Press, Oxford, 1987.

The reviews cited in the individual sections are also comprehensive. A useful recent reference on coordination polymers, metal-organic frameworks, and related topics is S. R. Batten, S. M. Neville, and D. R. Turner, *Coordination Polymers*, RSC Publishing, Cambridge, UK, 2009. *Chemical Reviews*, **2012**, volume 112, issue 2 is devoted to Metal-Organic Frameworks. *Dalton Transactions*, **2012**, issue 14 is devoted to Coordination Chemistry in the Solid State.

## Problems

- 9.1 By examining the symmetry, determine if any of the first four proposed structures for hexacoordinate complexes in Figure 9.3 would show optical activity.
- 9.2 Give chemical names for the following:
- $[\text{Fe}(\text{CN})_2(\text{CH}_3\text{NC})_4]$
  - $\text{Rb}[\text{AgF}_4]$
  - $[\text{Ir}(\text{CO})\text{Cl}(\text{PPh}_3)_2]$  (two isomers)
  - $[\text{Co}(\text{N}_3)(\text{NH}_3)_5]\text{SO}_4$
  - $[\text{Ag}(\text{NH}_3)_2][\text{BF}_4]$
- 9.3 Give chemical names for the following:
- $[\text{V}(\text{C}_2\text{O}_3)_3]^{3-}$
  - $\text{Na}[\text{AlCl}_4]$
  - $[\text{Co}(\text{en})_2(\text{CO}_3)]\text{Cl}$
  - $[\text{Ni}(\text{bipy})_3](\text{NO}_3)_2$
  - $\text{Mo}(\text{CO})_6$
- 9.4 Give chemical names for the following:
- $[\text{Cu}(\text{NH}_3)_4]^{2+}$
  - $[\text{PtCl}_4]^{2-}$
  - $\text{Fe}(\text{S}_2\text{CNMe}_2)_3$
  - $[\text{Mn}(\text{CN})_6]^{4-}$
  - $[\text{ReH}_9]^{2-}$
- 9.5 Name all the complexes in Problem 9.12, omitting isomer designations.
- 9.6 Name all the complexes in Problem 9.19, omitting isomer designations.
- 9.7 Give structures for the following:
- Bis(en)Co(III)- $\mu$ -amido- $\mu$ -hydroxobis(en)Co(III) ion
  - DiaquadiiododinitritoPd(IV), all isomers
  - $\text{Fe}(\text{dte})_3$ , all isomers

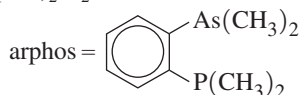


- 9.8 Show structures for the following:
- Triammineaquadichlorocobalt(III) chloride, all isomers
  - $\mu$ -oxo-bis[pentaamminechromium(III)] ion
  - Potassium diaquabis(oxalato)manganate(III)
- 9.9 Show structures for the following:
- cis-Diamminebromochloroplatinum(II)
  - Diaquadiiododinitritopalladium(IV), all ligands *trans*
  - Tri- $\mu$ -carbonylbis(tricarbonyliron(0))
- 9.10 Glycine has the structure  $\text{NH}_2\text{CH}_2\text{COOH}$ . It can lose a proton from the carboxyl group and form chelate rings bonded through both the N and one of the O atoms. Draw structures for all possible isomers of tris(glycinato)cobalt(III).

**9.11** Sketch structures of all isomers of  $M(AB)_3$ , in which AB is a bidentate unsymmetrical ligand, and label the structures *fac* or *mer*.

**9.12** Sketch all isomers of the following. Indicate clearly each pair of enantiomers.

- $[Pt(NH_3)_3Cl_3]^+$
- $[Co(NH_3)_2(H_2O)_2Cl_2]^+$
- $[Co(NH_3)_2(H_2O)_2BrCl]^+$
- $[Cr(H_2O)_3BrCl]^+$
- $[Pt(en)_2Cl_2]^{2+}$
- $[Cr(o\text{-phen})(NH_3)_2Cl_2]^+$
- $[Pt(bipy)_2BrCl]^{2+}$
- $Re(arphos)_2Br_2$



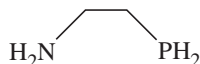
i.  $Re(dien)Br_2Cl$

**9.13** Determine the number of stereoisomers for the following. Sketch these isomers, and identify pairs of enantiomers. ABA, CDC, and CDE represent tridentate ligands.

- $M(ABA)(CDC)$
- $M(ABA)(CDE)$

**9.14** In Table 9.6 the number of stereoisomers for the formula  $M(ABC)_2$  where ABC is a tridentate ligand is given as 11, including five pairs of enantiomers. However, not all literature sources agree. Use sketches and models to verify (the authors hope!) the numbers cited in the table.

**9.15** The (2-aminoethyl)phosphine ligand has the structure shown below; it often acts as a bidentate ligand toward transition metals. (See N. Komine, S. Tsutsuminai, M. Hirano, S. Komiya, *J. Organomet. Chem.*, **2007**, 692, 4486.)



- When this ligand forms monodentate complexes with palladium, it bonds through its phosphorus atom rather than its nitrogen. Suggest an explanation.
  - How many possible isomers of dichlorobis[(2-aminoethyl)phosphine]nickel(II), an octahedral coordination complex in which (2-aminoethyl)phosphine is bidentate, are there? Sketch each isomer, and identify any pairs of enantiomers.
  - Classify the configuration of chiral isomers as  $\Lambda$  or  $\Delta$ .
- 9.16** An octahedrally coordinated transition metal M has the following ligands:  
Two chloro ligands  
One (2-aminoethyl)phosphine ligand (see Problem 9.15)  
One  $[O-CH_2-CH_2-S]^{2-}$  ligand

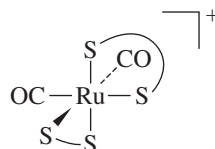
- Sketch all isomers, clearly indicating pairs of enantiomers.
  - Classify the configuration of chiral isomers as  $\Lambda$  or  $\Delta$ .
- 9.17** Suppose a complex of formula  $[Co(CO)_2(CN)_2Br_2]^-$  has been synthesized. In the infrared spectrum, it shows two bands attributable to C—O stretching but only one band

attributable to C—N stretching. What is the most likely structure of this complex? (See Section 4.4.2.)

**9.18** How many possible isomers are there of an octahedral complex having the formula  $M(ABC)(NH_3)(H_2O)Br$ , where ABC is the tridentate ligand  $H_2N-C_2H_4-PH-C_2H_4-AsH_2$ ? How many of these consist of pairs of enantiomers? Sketch all isomers, showing clearly any pairs of enantiomers. The tridentate ligand may be abbreviated as N—P—As for simplicity.

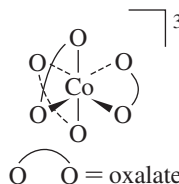
**9.19** Assign absolute configurations ( $\Lambda$  or  $\Delta$ ) to the following:

a.



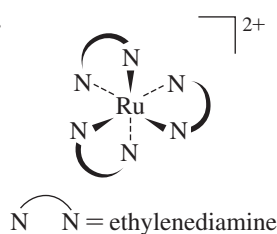
S—S = dimethyldithiocarbamate

b.



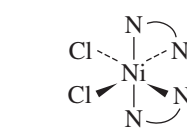
O—O = oxalate

c.



N—N = ethylenediamine

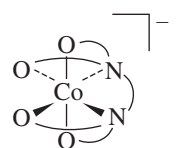
d.



N—N = 2,2'-bipyridine

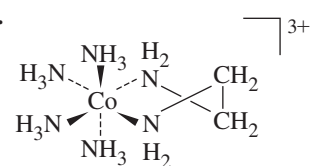
**9.20** Which of the following molecules are chiral?

a.

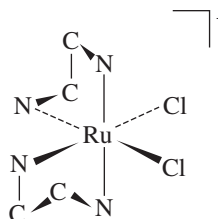


Ligand = EDTA

b.



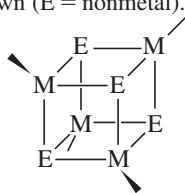
c.



Hydrogens omitted for clarity

**9.21** Give the symmetry designations ( $\lambda$  or  $\delta$ ) for the chelate rings in Problem 9.20b and 9.20c.

- 9.22** Numerous compounds containing central **cubane** structures, formally derived from the cubic organic molecule cubane,  $C_8H_8$ , have been prepared. The core structures typically have four metals at opposite corners of a distorted cube, with nonmetals such as O and S at the other corners, as shown (E = nonmetal).

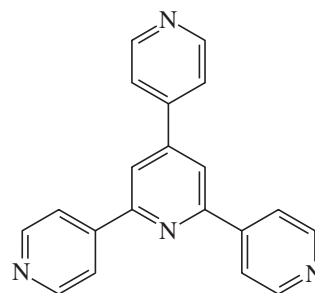
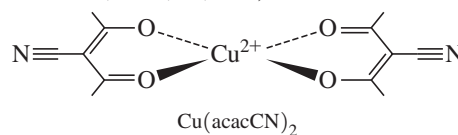


In addition to cubanes in which all metals and nonmetals are identical, they have been prepared with more than one metal and/or more nonmetal in the central 8-atom core; attached groups on the outside may also vary.

- How many isomers are possible if the core has the following formulas:
    - $Mo_3WO_3S$ ?
    - $Mo_3WO_2S_2$ ?
    - $CrMo_2WO_2SSe$ ?
  - Assign the point groups for each isomer identified in part a.
  - Is it possible for the central 8-atom core of a cubane structure to be chiral? Explain.
- 9.23** When  $cis-OsO_2F_4$  is dissolved in  $SbF_5$ , the cation  $OsO_2F_3^+$  is formed. The  $^{19}F$  NMR spectrum of this cation shows two resonances, a doublet and a triplet having relative intensities of 2:1. What is the most likely structure of this ion? What is its point group? (See W. J. Casteel, Jr., D. A. Dixon, H. P. A. Mercier, G. J. Schrobilgen, *Inorg. Chem.*, **1996**, 35, 4310.)
- 9.24** When solid  $Cu(CN)_2$  was ablated with 1064 nm laser pulses, various ions containing 2-coordinate  $Cu^{2+}$  bridged by cyanide ions were formed. These ions collectively have been dubbed a metal cyanide “abacus.” What are the likely structures of such ions, including the most likely geometry around the copper ion? (See I. G. Dance, P. A. W. Dean, K. J. Fisher, *Inorg. Chem.*, **1994**, 33, 6261.)
- 9.25** Complexes with the formula  $[Au(PR_3)_2]^+$ , where R is mesityl, exhibit “propeller” isomerism at low temperature as a consequence of crowding around the phosphorus. How many such isomers are possible? (See A. Bayler, G. A. Bowmaker, H. Schmidbaur, *Inorg. Chem.*, **1996**, 35, 5959.)
- 9.26** One of the more striking hydride complexes is  $[ReH_9]^{2-}$ , which has tricapped trigonal prismatic geometry (Figure 9.35c). Construct a representation using the hydrogen orbitals as a basis. Reduce this to its component irreducible representations, and indicate which orbitals of Re are of suitable symmetry to interact with the hydrogen orbitals.
- 9.27** The chromium(III) complex  $[Cr(bipy)(ox)_2]^-$  can act as a metalloligand to form a coordination polymer chain with Mn(II) ions, in which each manganese ion is 8-coordinate

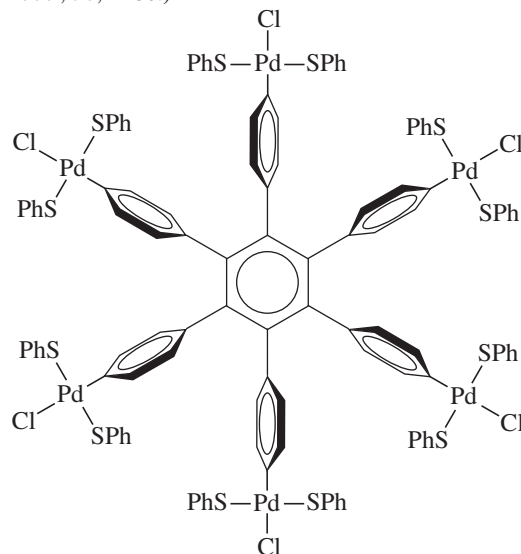
(in flattened square-antiprism geometry) and bridges four  $[Cr(bipy)(ox)_2]^-$  units; the ratio of Mn to Cr is 1:2. Sketch two units of this chain. (See F. D. Rochon, R. Melanson, M. Andruh, *Inorg. Chem.*, **1996**, 35, 6086.)

- 9.28** The metalloligand  $Cu(acacCN)_2$  forms a two-dimensional “honeycomb” sheet with 2',4',6'-tri(pyridyl)triazine (tpt); each honeycomb “cell” has sixfold symmetry. Show how six metalloligands and six tpt molecules can form such a structure. (See J. Yoshida, S.-I. Nishikiori, R. Kuroda, *Chem. Lett.*, **2007**, 36, 678.)



tpt

- 9.29** Determine the point groups:
- $Cu(acacCN)_2$  and tpt in Problem 9.28. (Assume delocalization of electrons in the  $O \cdots O$  part of the acacCN ligands and in the aromatic rings of tpt.)
  - A molecular cartwheel (note orientation of rings). (See H. P. Dijkstra, P. Steenwinkel, D. M. Grove, M. Lutz, A. L. Spek, G. van Koten, *Angew. Chem., Int. Ed.*, **1999**, 38, 2186.)



- 9.30** The separation of carbon dioxide from hydrogen gas is a promising industrial application of MOFs. A variety of metal-organic frameworks (MOF-177, Co(BDP), Cu-BTTri, and Mg<sub>2</sub>(dobdc)) were screened to assess their relative abilities for adsorption of these gases at partial pressures up to 40 bar and at 313 K (Z. R. Herm, J. A. Swisher, B. Smit, R. Krishna, J. R. Long, *J. Am. Chem. Soc.*, **2011**, *133*, 5664). Which gas, CO<sub>2</sub> or H<sub>2</sub>, is adsorbed more effectively by all four MOFs? Which two metal-organic framework properties most strongly correlate with CO<sub>2</sub> adsorption capacity? Tabulate the data quantifying these properties for these four MOFs. Which MOF adsorbed the most CO<sub>2</sub> at 5 bar? To what structural feature was this high adsorption at low pressures attributed? Which of these MOFs were identified as the best prospects for CO<sub>2</sub>/H<sub>2</sub> separation?
- 9.31** The capture of CO<sub>2</sub> by MOFs from post-combustion gas mixtures has been proposed to reduce CO<sub>2</sub> emissions from coal-fired power plants. The challenge is to engineer MOFs that will selectively adsorb CO<sub>2</sub> from these mixtures at relatively low temperatures and pressures, and subsequently permit facile CO<sub>2</sub> removal to regenerate the MOF for re-use. Describe the synthetic strategy used in T. M. McDonald, W. R. Lee, J. A. Mason, B. M. Wiers, C. S. Hong, J. R. Long, *J. Am. Chem. Soc.*, **2012**, *134*, 7056 to prepare MOFs with excellent CO<sub>2</sub> adsorption capability. Why do these MOFs require “activation,” and how is this carried out? Why were early attempts with M<sub>2</sub>(dobdc) likely unsuccessful, and how did this inform the design of a new MOF linker?
- 9.32** The exceptional stability of metal-organic frameworks containing Zr(IV) render them attractive for applications. One strategy for tuning MOF properties is to incorporate additional metals into the framework. Discuss the metalation options for MOF-525 and MOF-545 attempted in W. Morris, B. Voloskiy, S. Demir, F. Gándara, P. L. McGrier, H. Furukawa, D. Cascio, J. F. Stoddart, O. M. Yaghi, *Inorg. Chem.*, **2012**, *51*, 6443. Draw the structure of the linker that permits metal incorporation. How are MOF-525 and MOF-545 similar in their ability to be metalated? How are they different?