

Development of a New Data Format To Allow the Study of Structural Diversity and Ligand Behavior in Transition Metal Coordination Complexes Retrieved from the Cambridge Structural Database

N. D. Wright,* D. C. Povey, and B. J. Howlin

Structural and Computational Chemistry Group, Department of Chemistry, University of Surrey,
Guildford, Surrey GU2 5XH, United Kingdom

Received May 18, 1993*

A new structural representation is presented for transition metal coordination complexes, allowing a greater level of organizational hierarchy than that available in a conventional connection table. A computer program is used to transform data retrieved from the Cambridge Structural Database into the new file format, providing a rotational basis for systematic geometrical (and crystallographic) classification and analysis of metal complexes in a manner not currently possible.

INTRODUCTION

With the cost of designing new drug molecules ever escalating, organic chemists have been driven to develop and utilize sophisticated computational techniques to drive their research efforts along pathways of promise in an ever more logical process. In contrast, the design of inorganic materials, and in particular those of organometallic or coordination compounds, is still at a comparatively rudimentary level with a considerably less well developed arsenal of tools to aid in the research process.

A number of factors are responsible for the comparative lack of progress in our ability to model coordination compounds. Molecular mechanics describes the energy of a molecular system in terms of classical physical forces such as bond-stretching and angle and torsion angle bending, as well as electrostatic and steric terms. For purely organic species the parameter set is widely documented and readily applicable to calculations on a vast number of different compounds. In the case of coordination compounds, the parametrization process is complicated by the wide range of geometries (octahedral, tetrahedral, etc.), coordination numbers, and oxidation states possible for transition metals.¹⁻³ As a result it is difficult to find transferable interatomic potentials and force constants. Quantum mechanical calculations have had limited application; the presence of full or partially filled d- and f-orbitals in transition metal compounds requires that the basis functions describing the wave function are carefully chosen in order to obtain a balance between accuracy and the computational resources necessary. Among the basis sets developed,⁴ the use of SINDO⁵ in particular is beginning to have an impact on the scale of computations now possible.

With these restrictions placed on the traditional computational tools, we are led to examine new directions to aid in our understanding of such compounds and their structures. In other areas of chemistry an enhanced knowledge of the structure of known compounds has been of use in the prediction of new structures. For example, in the protein folding problem, a knowledge of the secondary structure of known sequences of amino acids is used as a basis for the prediction of the structure of an unknown or modified sequence.⁶ Our aim is to generate a suitable representation for coordination complexes in which the metal of a mononuclear structure forms the focal point and the remainder of the connectivity table is

partitioned into ligand subsets. Such a representation then permits a searchable classification and metal complexes and a rational basis for systematic geometrical (and crystallographic) analyses based on data obtained from the Cambridge Structural Database^{7,8} in a way not currently possible.

Cambridge Structural Database The Cambridge Structural Database (CSD) is an invaluable store of computer readable structural and bibliographic information for over 100 000 compounds determined by X-ray and neutron diffraction methods. The provision of powerful search and analysis software (QUEST-3D and GSTAT) have made the CSD more than just a good depository of such structural information. Initially, use of the database led to the development of a table of standardized bond lengths for use in molecular mechanics calculations. This table has recently been updated to provide even more reliable values for organic species⁹ and for organometallics and coordination complexes.¹⁰ As the number of database entries has grown, the study of molecular fragments and conformation has become practical.¹¹⁻¹⁴ We are able not only to retrieve structural information but to use sophisticated analytical tools to compare structural fragments and thus to enhance our understanding of 3D chemistry. This chemical knowledge is then available to provide a firm basis for rational methods of molecular design.

We can, for example, easily construct a connectivity-based search query to retrieve all of the octahedral complexes containing the ethylenediamine (en) ligand from the database. Such queries are possible because we are searching for a specific fragment or fragment type which can be clearly defined. More general searches are unfortunately more difficult since they can return large amounts of unwanted information, often leading to the need for laborious manual intervention to extract the data of interest. For example, it is very difficult to code a query (or a series of queries) that would enable the retrieval of all entries containing octahedrally coordinating bidentate ligands. The concept of a "ligand" is only present in the form of a very limited number of chemical classes (i.e. chemical class 76 contains complexes of ethylenediamine.) Additionally and more significantly, the geometric (stereochemical) arrangement of individual ligands about a metal center in a complex is not explicitly stored within the database and must be derived from the atomic coordinates if required. Although the CSD is an excellent source of data, these weaknesses limit the extent to which we are able to use the CSD to study coordination compounds and the potential to generally improve our current modeling capabilities.

* Abstract published in *Advance ACS Abstracts*, January 15, 1994.

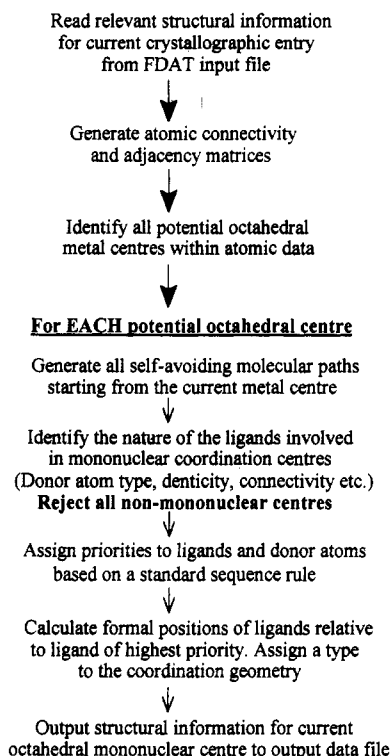


Figure 1. Schematic overview of the operation of the data-file generator.

PROGRAM DESIGN

We have developed a computer program using molecular graph theory to transform structural information retrieved from the Cambridge Structural Database into a new data format specifically designed for mononuclear coordination compounds. At the center of this new format is a means of structural description whereby the metal center of a complex forms a focal point with the remainder of the connectivity table separated into ligand subsets. A geometrical description of the spatial arrangement of ligands about the metal center is included, providing a rational basis for systematic geometrical and crystallographic analyses of currently available data. Retention of the CSD refcode within the new format provides a means of reference back to the main database for conventional data analysis. All program code has been written in FORTRAN-77 and runs on a Micro VAX computer running under the VMS operating system. A schematic overview of the operation of this data-file generator is given in Figure 1. The important steps are described in greater detail for the case of *octahedral* species together with a description of the data file format. Other mononuclear coordination geometries (tetrahedral, square-planar, etc.) are processed in a similar manner to the octahedral case outlined below.

Source of Structural Data. A conventional QUEST search is used to generate an FDAT¹⁵ file containing all structures found to possess one or more six-coordinate metal centers. At this stage conventional QUEST search screens may be used to restrict output to a narrower field if required, i.e. structures having an acceptable crystallographic *R*-factor value, or to exclude all structures marked with an error flag. This FDAT file, containing both connectivity and crystallographic information, is then used as the input for our procedure. The initial QUEST search retrieves all octahedral centers for subsequent examination, but in this application we are only considering the mononuclear species. Dimeric and polymeric structures, often with metal-metal bonds, require a different classification and are not considered in this study. These

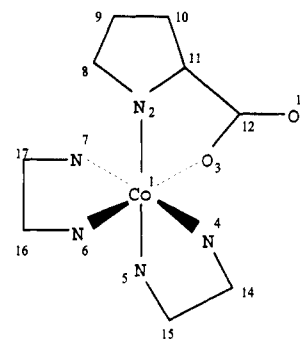


Figure 2. Schematic structure and corresponding atom numbering scheme of the bis(ethylenediamine-*N,N'*)(pyrrole-2-carboxylato-*N,O*)cobalt(III) octahedron.

unwanted structures can be discarded following an examination of generated molecular paths.

Molecular Path Analysis. It is necessary to generate all molecular paths for each metal center under consideration. Analysis of all the paths found starting with a particular metal center reveals the nature of the ligands coordinated and allows us to reject nonmononuclear metal centers from further processing.

The procedure used for generating all self-avoiding molecular paths is a simple one as outlined by Randic.¹⁶ The connectivity information retrieved from the input FDAT file is converted into an adjacency matrix for all non-hydrogen atoms, which is then searched for nonzero entries in a systematic manner. We start with the current metal center and search the adjacency matrix to determine all possible molecular paths. Figure 2 illustrates the schematic structure of an example metal complex and the corresponding atomic numbering scheme adopted. The molecular paths generated for this basic structure (ligating atoms are highlighted in bold type) are as follows:

```

Co(1)-N(2)-C(11)-C(12)-O(3)
Co(1)-N(2)-C(11)-C(12)-O(13)
Co(1)-N(2)-C(11)-C(10)-C(9)-C(8)
Co(1)-N(2)-C(8)-C(9)-C(10)-C(11)
Co(1)-N(2)-C(8)-C(9)-C(10)-C(11)-C(12)-O(3)
Co(1)-N(2)-C(8)-C(9)-C(10)-C(11)-C(12)-O(13)
Co(1)-O(3)-C(12)-O(13)
Co(1)-O(3)-C(12)-C(11)-N(2)
Co(1)-O(3)-C(12)-C(11)-C(10)-C(9)-C(8)-N(2)
Co(1)-N(4)-C(14)-C(15)-N(5)
Co(1)-N(5)-C(15)-C(14)-N(4)
Co(1)-N(6)-C(16)-C(17)-N(7)
Co(1)-N(7)-C(17)-C(16)-N(6)
  
```

For more complicated structures a much larger number of paths may be generated. As a result of memory restrictions on our current computer, we are unable to handle structures generating over 2000 paths for a given metal center. The CSD refcode for oversized structures is stored in an error file for reference. Experience has shown a very large proportion of these structures to be polynuclear and as such outside our current area of interest.

Determination of Ligand Structure. Path arrays are kept in memory in the order of the ligating atoms. Thus all paths

(a)

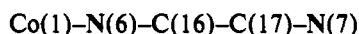
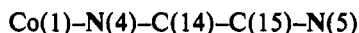
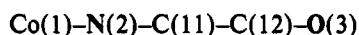
Co	N	O	N	N	N	N	C	C	C	C	O	C	C	C	C
0	1	1	1	1	1	1	0	0	0	0	0	0	0	0	0
1	0	0	0	0	0	0	1	0	0	1	0	0	0	0	0
1	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0
1	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0
1	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0
1	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0
1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1
0	1	0	0	0	0	0	0	1	0	0	0	0	0	0	0
0	0	0	0	0	0	0	1	0	1	0	0	0	0	0	0
0	0	0	0	0	0	0	0	1	0	1	0	0	0	0	0
0	1	0	0	0	0	0	0	0	1	0	1	0	0	0	0
0	0	1	0	0	0	0	0	0	0	1	0	1	0	0	0
0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0
0	0	0	1	0	0	0	0	0	0	0	0	0	1	0	0
0	0	0	0	1	0	0	0	0	0	0	0	0	0	1	0
0	0	0	0	0	1	0	0	0	0	0	0	0	0	0	1
0	0	0	0	0	0	1	0	0	0	0	0	0	0	1	0

(b)

N	C	C	N
0	1	0	0
1	0	1	0
0	1	0	1
0	0	1	0

Figure 3. Adjacency matrix (a) for all non-hydrogen atoms in the bis(ethylenediamine-*N,N'*)(pyrrole-2-carboxylato-*N,O*)cobalt(III) octahedron and (b) for one of the ethylenediamine ligands.

for a particular metal-donor atom pair are stored together. From this information the nature of the ligands present can be determined. The first step is to reduce the number of paths to six, one for each donor atom. Only the "best" path is kept for each donor atom. This is achieved by considering the number of donor atoms located in each path, and the length of the path, so as to keep the path most representative of the ligand in question. For paths containing more than one donor atom we keep the shortest path as this represents best the structure of the chelate ring. Where multidentate ligands are present, the relevant donor atoms are found in more than one molecular path. Further examination allows the number of paths to be reduced so that each of the six donor atoms occurs only once. Where two or more paths contain the same number of donor atoms and chelate ring size, it is arbitrary as to which path is retained. In the example given in Figure 2 the number of paths is reduced to three, one path per ligand (all bidentate):



These paths are representative only of the structure of the chelate ring and not of the full ligand. With a knowledge of the donor atoms present in a ligand, we refer back to the full list of paths to enable a connectivity table to be derived for the complete structure of each ligand. All paths involving each donor atom in the ligand are examined and any atoms encountered added to the connectivity list for the current ligand. Atoms are renumbered, and a ligand adjacency matrix is generated. Figure 3a shows the full adjacency matrix for all non-hydrogen atoms in bis(ethylenediamine-*N,N'*)(pyrrole-2-carboxylato-*N,O*)cobalt(III). An adjacency matrix for one of the ethylenediamine ligands is given in Figure 3b. This ligand connectivity information is stored in the output data file to enable searching based on the structure of individual ligands.

Assignment of Ligand Priority. Each ligand is assigned a priority within each structure processed according to a standard sequence rule. The sequence rule adopted is based on the

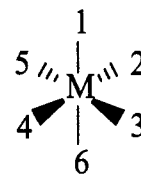


Figure 4. Formal numbering scheme adopted for a metal octahedron.

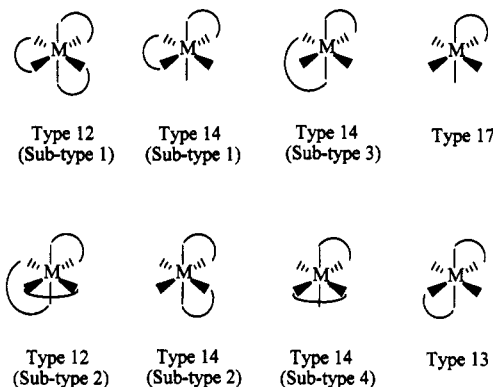


Figure 5. Geometric types and subtypes assigned for octahedral complexes containing monodentate and bidentate ligands.

standard method used in assigning stereochemical notation to coordination compounds within the *Chemical Abstracts* system.¹⁷ The rule in essence is as follows: (1) Ligands of higher liganacy (denticity) are of higher precedence; (2) higher atomic number precedes lower. In the case of an octahedral center with the ligands ethylenediamine, Cl, Br, Cl, and H₂O, the ethylenediamine ligand is of highest priority (bidentate ligand > monodentate) and the monodentate ligands according to atomic number (Br > Cl > H₂O). At present we have not extended this classification process to further differentiate ligands according to chiral or stereochemical aspects, and this remains a matter for future consideration. Complexes with multidentate ligands frequently require the differentiation of identical donor atoms. When this is the case, it is necessary to consider the substituents in a tree-based depthwise examination when one is assigning priority using a similar sequence rule to that described above.

Assignment of a Geometric Type. To allow later comparison of structures with a similar coordination geometry, each octahedron encountered is classified by assigning a number to identify its geometric type. A subtype number is also assigned to allow geometric isomers of the same type to be differentiated if required.

In order to assign a geometric type it is necessary to adopt a particular formal numbering scheme for an octahedron. All structures are oriented so as to locate the donor atom of highest priority into formal position 1 (see Figure 4) and the second highest into formal position 2. All other donor atoms can now be assigned a formal position within the octahedron. This serves to restrict the number of ligand arrangements possible and enables easier geometric classification. The geometric types possible for complexes containing only monodentate and bidentate ligands are shown in Figure 5. For a complex containing six monodentate ligands only one type is possible (type 18), whereas with two bidentate and two monodentate ligands two distinct forms are possible, with the bidentate

```
#GEWVAF 1 2 14P21/n R=0.0430 11765 74784 17840 90 9787 90 343020
CO 1 13 34447. 14645. 7238.1a 5N 1b 3O 2a 11N 3a 16N 3a 15N 2a 12N 12-1
12 O 1 3N 3 5 5 3 0 0 2 0 0 2513 212 7
2 45340. 22480. 820. 23720. 27620. 340.
1010 4 4 5 5 3 5 6 3 7 8
8 8O O N C C C C C
22 N 1 11N 2 12 11 12 0 0 2 0 0 2222 112 9
2 36910. 35930. 13560. 47400. 4680. 14020.
6 6 3 4 1 2 3 4
4 4N N C C
32 N 1 15N 2 16 15 16 0 0 2 0 0 2222 110 12
2 32060. -7540. 1490. 23050. 5110. 13100.
6 6 3 4 1 2 3 4
4 4N N C C
```

Figure 6. Example data entry for the bis(ethylenediamine-*N,N'*)(pyrrole-2-carboxylato-*N,O*)cobalt(III) octahedron converted from CSD entry #GEWVAF.

a

```
#GEWVAF 23890523 21 9 28 0 0 2 6 41 0 0 47132100000020000000000088
11765 74784 17840 90 9787 90343020 1 6 2 0 1 0 0153 14P21/n 440
R=0.0430 Paper gives beta 17.87(1)
211 0121 0112 0011 6121 6110 6
C 68H 23CL 99CO133N 68O 68
CO1 34447 14645 7238 CL1 -12649 62580 -21575 O1 45340 22480 820
O2 46840 36500 -9980 N1 23720 27620 340 C1 40910 31840 -5000
C2 28820 35450 -5320 C3 20650 44430 -10240 C4 10270 41990 -7500
C5 12430 31640 -960 N2 36910 35930 13560 N3 47400 4680 14020
C6 44430 31680 20650 C7 53450 19400 18510 N4 32060 -7540 1490
N5 23050 5110 13100 C8 25350 -20230 5380 C9 16680 -9670 8890
O3 12100 78100 -24860 O4 76970 -360 14140 H1 21900 50960 -14630
H2 3030 46540 -9680 H3 6840 27990 2100 H4 47830 42280 22870
H5 40170 25960 24120 H6 58320 25610 15560 H7 57900 14740 22920
H8 21600 -28550 1850 H9 30250 -26460 9180 H10 11020 -5020 5080
H11 13110 -16980 12240 H12 40040 44000 11180 H13 30490 39690 14600
H14 52000 -450 11420 H15 44950 -2860 16980 H16 28470 -5280 -2870
H17 38530 -12160 1040 H18 18380 13350 13890 H19 26390 1200 17310
H20 9300 82560 -29350 H21 80690 6160 18400
3 0 6 6 1 7 5 7 8 5 1 11112 1 115164041 8 910131314141717181111121215151616 0
0 91013141718
```

b

```
*REFC=GEWVAF // bis(Ethylenediamine-N,N')-(pyrrole-2-carboxylato-N,O)-cobalt chl
oride dihydrate // *FORM=C9 H19 Co1 N5 O2 1+,C11 1-,2(H2 O1) // *AUTH=A.Hammersh
oi,R.M.Hartshorn,A.M.Sargeson // *CODE=182(J.Chem.Soc.,Chem.Comm.) // *VOLUME= //
*PAGE= 1267 // *YEAR=1988 //
```

Figure 7. (a) CSD FDAT file entry for refcode #GEWVAF. (b) CSD journal file entry for refcode #GEWVAF.

ligands in a trans arrangement (type 13) or in a cis arrangement (type 14). With the latter, geometrical isomers are possible and a subtype is correspondingly assigned. Other types are available to classify complexes containing ligands of higher denticity.

At this stage of processing we are able to remove six-coordinate entries whose coordination geometry is distorted and cannot be classified as an octahedral structure. The CSD refcodes for these structures are stored in an error file for later reference if required. Structures other than octahedral (tetrahedral, square-planar, etc.) are processed similarly, and a number of type and subtype numbers are available with which to classify their structures.

Output Data File Format. The data format described in detail below has been specially designed to address the needs of an inorganic computational chemist. Structural information is stored not as a single connectivity matrix, as in the CSD, but is split into ligand and metal information for each octahedron present. The design adopted is flexible enough to allow modification at a later stage if necessary.

An example data entry for the CSD refcode #GEWVAF structure is given in Figure 6. (The corresponding CSD FDAT and journal file entries are shown in Figure 7a,b). The data are split into three main sections:

(1) *Complex Record.* This holds the original CSD refcode and crystallographic information (space group number/symbol, *R*-factor value, and the cell parameters).

(2) *Metal Record.* One record for each mononuclear octahedron is present and holds the metal atom type, original CSD atom number, and 3D coordinates, along with the geometrical type assigned to the octahedron.

(3) *Ligand Records.* For each metal record present, a number of ligand records are stored.

(a) *General Records.* These hold the ligand number, denticity, donor atom types, and original CSD atom numbers, along with the calculated ligand and donor atom priorities.

(b) *Coordinate Records.* These hold the donor atom coordinates.

(c) *Ligand Connectivity Records.* These hold a sequence of integers storing the ligand connectivity (as used in the CSD FDAT format).

(d) *Ligand Atom Type Records.* These hold the atom types corresponding to the connectivity integers stored in records 3c.

In addition to the geometrical type assignment, an encoded summary of the coordination geometry for each octahedron

Table I. Tabulation of the Occurrence of the Ethylenediamine (en) Ligand According to the Geometrical Coordination Type for Mononuclear Octahedral Metal Complexes

type	occurrence of hit structures		
	(en)	(en) ₂	(en) ₃
12	21	57	71
13		15	
14	1	113	
17	17		

is stored on the metal record. In the example data file highlighted above (Figure 6), the encoded summary for the cobalt octahedron in CSD refcode #GEWVAF is

1a 5N 1b 3O 2a 11N 3a 16N 3a 15N 2a 12N

Six characters are used to represent each formal position in the octahedron. Thus for formal position 1 we have 1a 5N. The first digit refers to the ligand number. The second character field is a priority symbol. Donor atoms of highest priority are assigned the letter *a*, atoms of next highest priority are assigned the letter *b*, etc. The next two digits are the donor atom number within the ligand connectivity table. Finally, the last field holds the two character atom type.

We have chosen to store coordinates for the central metal atom and the surrounding donor atoms. This was felt important to allow subsequent searches to be restricted by, or to allow output of, metal–donor bond lengths. Similarly, examination of metal–ligand bond lengths in different geometrical types, with reference also to the nature of the other ligands present, is possible if required. This is a potentially important step in the selection of improved bond lengths for molecular mechanics studies. Keeping all data tagged with the original CSD refcode allows the user to go back and analyze individual or groups of structures further, using the powerful GSTAT package if and when required.

Searching. An additional program has been developed to search the new data file. The menu driven interface allows the user to select a number of parameters as a search query. These parameters include the geometric structural type and subtype, the metal atom type, and various ligand features such as the denticity, donor atom type, and size of the chelate ring where applicable. Searches may also be established to locate all entries matching a particular search ligand. Reporting may be as simple as the CSD refcode for each hit or a user-selected tabulation of one or more parameters.

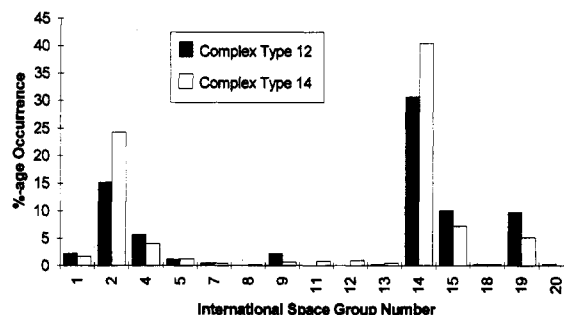
SPECIMEN RESULTS

To illustrate the potential applications made possible by using our new data format, we have chosen to present the results of a number of test runs, highlighting studies not previously possible. All searches have been carried out on a database derived from the January 1993 release of the CSD. QUEST was used to produce an FDAT file of octahedral metal centers, eliminated entries with an error flag set or no coordinate records present. A further restriction based on the crystallographic *R*-factor was not used as this information is retained in the output data format.

Analysis of Ligand Distribution of Complex Type. Inclusion within the data file of the absolute geometry of coordination allows an analysis of the conformation preferred by a ligand, as shown in Table I for all occurrences of the unsubstituted ethylenediamine ligand in complexes containing a mixture of bidentate and monodentate ligands. The results are further categorized to differentiate between cases with one, two, or three ethylenediamine ligands per metal complex. Such a

Table II. Tabulation of the Average Nickel–Oxygen Bond Length, Sample Standard Deviation (σ), and Number of Occurrences (n_{occ}) Located in a Search of Mononuclear Octahedral Metal Complexes with at Least One Acetylacetonate (acac) Ligand Present

type	Ni–O bond length		
	mean (Å)	σ	n_{occ}
(acac)	12	2.015	0.0001
	13		2
	14		
(acac) ₂	12		
	13	2.021	0.0125
	14	2.022	0.0372
(acac) ₃	12	2.043	0.0483
	13		6
	14		

**Figure 8.** Comparison of space group distribution for mononuclear octahedral metal complexes of types 12 and 14.

study is useful in examining preferences in complex geometry or highlighting uncommon structures for further examination.

Analysis of Metal–Ligand Bond Lengths or Angles. Using a conventional CSD GSTAT survey, we are able to tabulate metal–ligand donor atom bond lengths. Inclusion of metal and donor atom coordinates within the new data format permits the calculation of metal–donor atom bond lengths or angles for any hit structure according to the complex type. For example, in Table II we have tabulated average values of the nickel–oxygen bond length in octahedral nickel complexes of the acetylacetonate (acac) ligand. Once again the values are broken down by geometric type of complex and number of acac ligands per octahedron. Providing an easier means to analyze variations in metal–donor bond lengths and angles in this manner will aid in the improvement of the currently available molecular mechanics force field parameters. We are also able to relate distortions from ideal coordination geometry to the ligand types present.

Space Group Distribution. The data file format adopted includes much of the original crystallographic information from the CSD FDAT file and, in particular, the International Tables for Crystallography space group number.¹⁸ Figure 8 compares the percentage occurrence of mononuclear octahedral metal complexes of assigned types 12 and 14 having a space group number of 20 or lower. A study of this sort may be of use in outlining differences in packing preferences between structural types of subtypes. Ultimately we would like to be able to correlate molecular attributes with crystal parameters and develop an ability to engineer solid-state structure.

DISCUSSION

We have presented a method to reformat structural data obtained from the Cambridge Structural Database into a new data format specifically designed for coordination compounds. The inclusion of ligand connectivity and the assignment of a geometric type to the nature of the coordination present for

individual metal centers provides the opportunity to study the influence of ligand and metal factors on the resultant three-dimensional structure. In this manner the method provides a rapid way in which a knowledge of the structure of existing molecules may be made available to the molecular modeler to assist in conventional structural design processes. A database of easily accessible structural geometries provides a useful source of data for comparison and validation of results from techniques such as molecular mechanics or quantum mechanics.

We aim to extend the scope of the study and introduce geometric types to cover structures other than the mononuclear metal centers currently covered. Dimeric and polymeric structures are more diverse in structure and a large increase in types classifications is likely to be necessary in order to cover the field completely. It is envisaged that an automated, systematic analysis of the knowledge base will further assist in unlocking "rules" governing the structure of such compounds and a move toward more rational methods of structural design and modification.

ACKNOWLEDGMENT

This research was supported by the United Kingdom Science and Engineering Research Council in the form of a studentship (N.D.W.).

REFERENCES AND NOTES

- (1) Snow, M. R. Structure and Conformational Analysis of Coordination Complexes. The $\alpha\alpha$ Isomer of Chlorotetraethylenepentaminecobalt(III). *J. Am. Chem. Soc.* **1970**, *92*, 3610–2617.
- (2) Hancock, R. D. Molecular Mechanics Calculations as a Tool in Coordination Chemistry. *Prog. Inorg. Chem.* **1989**, *37*, 187–291.
- (3) Bernhardt, P. V.; Comba, P. Molecular Mechanics Calculations of Transition Metal Complexes. *Inorg. Chem.* **1992**, *31*, 2638–2644.
- (4) Hansen, L. M.; Marynick, D. S. Extended Basis Sets for the Transition Metals Yttrium through Cadmium. *J. Comput. Chem.* **1990**, *11* (4), 518–523.
- (5) Wasielewska, E.; Ilkowska, E. SINDO studies of $[M(CN)_5CO]^{4-}$ Complex Ions for M = Iron, Manganese and Chromium. *Polyhedron* **1993**, *12* (5), 461–465.
- (6) Blundell, T. L.; Carney, D.; Gardner, S.; Hayes, F.; Howlin, B.; Hubbard, T.; Overington, J.; Singh, D. A.; Sibanda, B. L.; Sutcliffe, M. Knowledge-Based Protein Modelling and Design. *Eur. J. Biochem.* **1988**, *172*, 513–520.
- (7) Allen, F. H.; Bellard, S. A.; Brice, M. D.; Cartwright, B. A.; Doubleday, A.; Higgs, H.; Hummelink, T.; Hummelink-Peters, B. G.; Kennard, O.; Motherwell, W. D. S.; Rodgers, J. R.; Watson, D. G. The Cambridge Crystallographic Data Centre: Computer-Based Search, Retrieval, Analysis and Display of Information. *Acta Crystallogr.* **1979**, *B35*, 2331–2339.
- (8) Allen, F. H.; Davies, J. E.; Galloy, J. J.; Johnson, O.; Kennard, O.; Macrae, C. F.; Mitchell, E. M.; Mitchell, G. F.; Smith, J. M.; Watson, D. G. The Development of Versions 3 and 4 of the Cambridge Structural Database System. *J. Chem. Inf. Comput. Sci.* **1991**, *31*, 187–204.
- (9) Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. Tables of Bond Lengths Determined by X-Ray and Neutron Diffraction. Part 1. Bond Lengths in Organic Compounds. *J. Chem. Soc., Perkin Trans. 2* **1987**, S1–S19.
- (10) Orpen, A. G.; Brammer, L.; Allen, F. H.; Kennard, O.; Watson, D. G.; Taylor, R. Tables of Bond Lengths Determined by X-Ray and Neutron Diffraction. Part 2. Organometallic Compounds and Co-ordination Compounds of the d- and f-Block Metals. *J. Chem. Soc., Dalton Trans.* **1989**, S1–S83.
- (11) Auf der Heyde, T. P. E.; Bürgi, H. B. Molecular Geometry of d⁸ Five-Coordination. 1. Data Search, Description of Conformation, and Preliminary Statistics. *Inorg. Chem.* **1989**, *28*, 3960–3969.
- (12) Auf der Heyde, T. P. E.; Bürgi, H. B. Molecular Geometry of d⁸ Five-Coordination. 2. Cluster Analysis, Archetypal Geometries and Cluster Statistics. *Inorg. Chem.* **1989**, *28*, 3970–3981.
- (13) Auf der Heyde, T. P. E.; Bürgi, H. B. Molecular Geometry of d⁸ Five-Coordination. 3. Factor Analysis, Static Deformations and Reaction Coordinates. *Inorg. Chem.* **1989**, *28*, 3982–3989.
- (14) Nørskov-Lauritsen, L.; Bürgi, H. B. Cluster Analysis of Periodic Distributions; Application to Conformational Analysis. *J. Comput. Chem.* **1985**, *6* (3), 216–228.
- (15) Cambridge Structural Database Version 4 Users Manual.
- (16) Randic, M.; Brissey, G. M.; Spencer, R. B.; Wilson, C. L. Search for All Self-avoiding Paths for Molecular Graphs. *Comput. Chem.* **1979**, *3*, 5–13.
- (17) Brown, M. F.; Cook, B. R.; Sloan, T. E. Stereochemical Notation in Coordination Chemistry. Mononuclear Complexes. *Inorg. Chem.* **1975**, *14*, 1273–1278.
- (18) Hahn, T., Ed. *International Tables for Crystallography. Space Group Symmetry*. Reidel: Dordrecht, The Netherlands, 1983; Vol. A.