

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/236585562>

# A simple method for drawing stereoisomers from mononuclear octahedral metal complex unit with monodentate ligands

ARTICLE *in* JOURNAL OF CHEMICAL EDUCATION · JANUARY 2008

Impact Factor: 1.11

---

READS

20

## 2 AUTHORS:



**Aminou Mohamadou**

Université de Reims Champagne-Ardenne

63 PUBLICATIONS 597 CITATIONS

SEE PROFILE



**Arnaud Haudrechy**

Université de Reims Champagne-Ardenne

60 PUBLICATIONS 622 CITATIONS

SEE PROFILE

# A Simple Method For Drawing Chiral Mononuclear Octahedral Metal Complexes

Aminou Mohamadou and Arnaud Haudrechy\*

ICMR (Institut de Chimie Moléculaire de Reims), Université de Reims Champagne-Ardenne, Faculté des Sciences, Moulin de la Housse, BP 1039, 51687 Reims Cedex 2, France; \*arnaud.haudrechy@univ-reims.fr

It is well-known that octahedral transition-metal complexes are involved in a number of mechanisms in organic synthesis. In the case of asymmetric inductions, many authors choose to ignore the chiral octahedral metal center in the reaction mechanism. The octahedral metal complexes thus formed can be responsible for recognition phenomena. For example, a chiral inductor chelating in an octahedral network transmits its information and creates diastereoisomeric structures. Ideally, these species should be observed one-by-one to identify which is the real actor (ligands or metallic ion) in the asymmetric process.

Octahedral coordination, being the most frequent geometry for metallic centers, is the most studied with regard to the topographical stereochemistry. According to the number of different ligands, octahedral coordination units with at least two different monodentate ligands can give a series of ten possible complexes that can be classified into five families: (I) bis-heteroleptic complexes (two ligands **A** and **B**); (II) tris-heteroleptic complexes (three ligands **A**, **B**, and **C**); (III) tetrakis-heteroleptic complexes (four ligands **A**, **B**, **C**, and **D**); (IV) pentakis-heteroleptic complexes (five ligands **A**, **B**, **C**, **D**, and **E**); and (V) hexakis-heteroleptic complexes (six ligands **A**, **B**, **C**, **D**, **E**, and **F**).

Even though such an assessment remains problematic in reality, we would like, in this didactical article, to show an easy way to draw all of these octahedral complexes.<sup>1</sup>

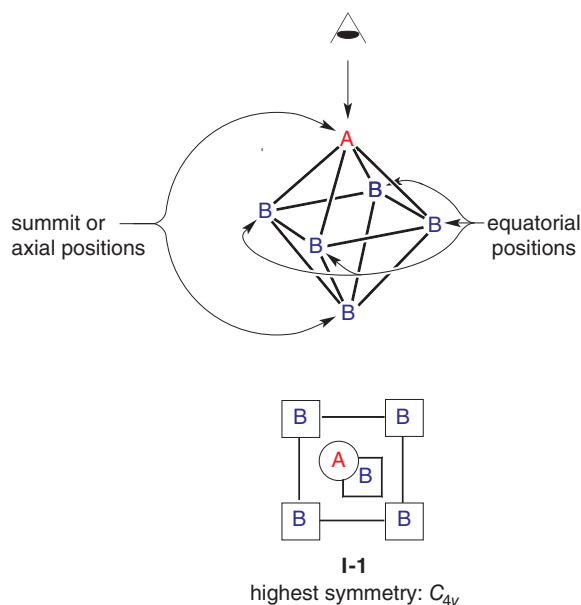


Figure 1. Bis-heteroleptic complexes: 1A-5B.

## Bis-Heteroleptic Complexes

There are three possible octahedral complexes with two different monodentate ligands **A** and **B**:  $[M(A)(B)_5]$ ,  $[M(A)_2(B)_4]$ , and  $[M(A)_3(B)_3]$ .

### One Ligand **A**, Five Ligands **B**

A possible ligand array around the metal is drawn in structure I-1 (Figure 1) with the Newman projection appearing below it.

### Two Ligands **A**, Four Ligands **B**

The two ligands **A** can adopt two relative positions (commonly cis or trans). They can be placed in opposite adjacent positions (I-2a) or on axial positions (I-2b) (Figure 2).

### Three Ligands **A**, Three Ligands **B**

With this kind of complex, the problem can be progressively examined using the two cases seen in the preceding paragraph (representations I-2a and I-2b). In the first case (Figure 3), starting from representation I-2a, a ligand **A** can occupy one position in the equatorial plane of the octahedron (representation I-3a) or an axial position (representation I-3b).

In conclusion for part I, we note that the octahedral complexes with two different monodentate ligands possess only four

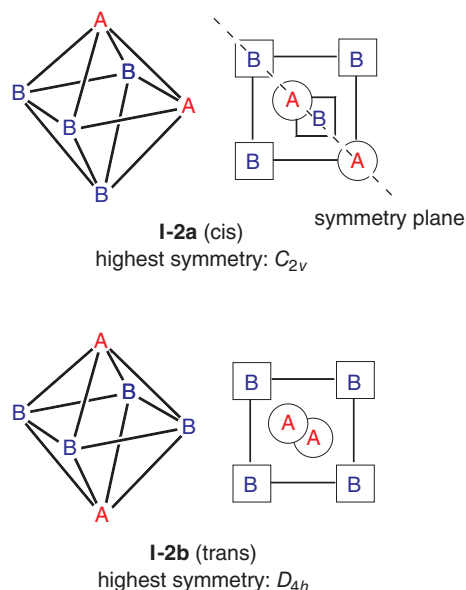


Figure 2. Bis-heteroleptic complexes: 2A-4B.

diastereoisomers. Thus, an asymmetrical reaction can only be achieved through the use of an external chiral induction.

### Tris-Heteroleptic Complexes

There are three possible octahedral complexes with three different monodentate ligands **A**, **B**, and **C**:  $[M(A)(B)(C)_4]$ ,  $[M(A)(B)_2(C)_3]$ , and  $[M(A)_2(B)_2(C)_2]$ .

#### One Ligand **A**, One Ligand **B**, Four Ligands **C**

When ligand **A** is placed in one of the axial positions (Figure 4), the other axial position can be occupied by ligand **B** (representation II-1a) or ligand **C** (representation II-1b).

#### One Ligand **A**, Two Ligands **B**, Three Ligands **C**

As in the preceding paragraph, two axes are considered, **A-B** and the **A-C**. In the case where **A** and **B** occupy the axial positions, it is obvious that the second ligand **B** is in an equatorial position (representation II-2a in Figure 5).

In the case where ligand **A** and one of the ligands **C** are in the axial positions, the two ligands **B** can be placed in the equatorial plane in two ways (Figure 5): (i) the two ligands **B** are in cis positions (representation II-2b) or (ii) they are in trans positions (representation II-2c).

#### Two Ligands **A**, Two Ligands **B**, Two Ligands **C**

With this new case, we are now entering into the magic world of chirality. Following the progressive approach applied in the preceding paragraphs and knowing that in an octahedron there are three possibilities to put two ligands in trans positions, let us consider the three viewing possibilities through an **A-A** axis, an **A-B** axis, and an **A-C** axis. Only the Newman projections will be used to describe these octahedral complexes.

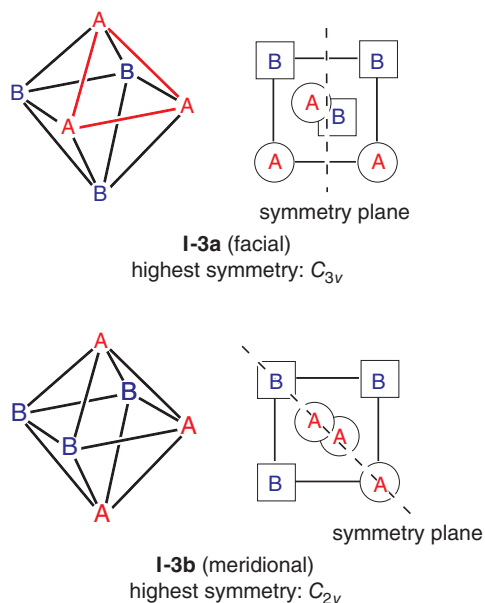


Figure 3. Bis-heteroleptic complexes: 3A-3B.

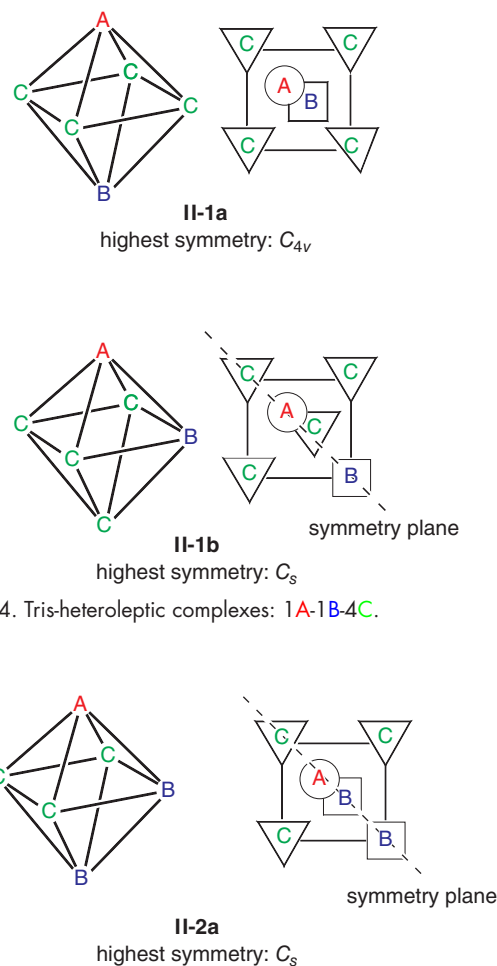


Figure 4. Tris-heteroleptic complexes: 1A-1B-4C.

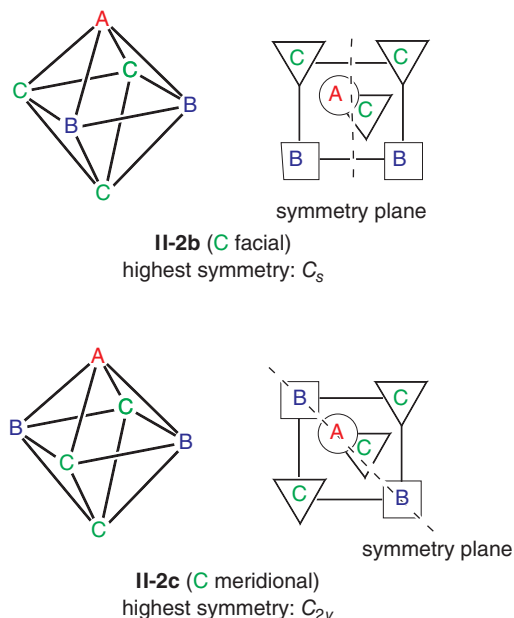


Figure 5. Tris-heteroleptic complexes: 1A-2B-3C.

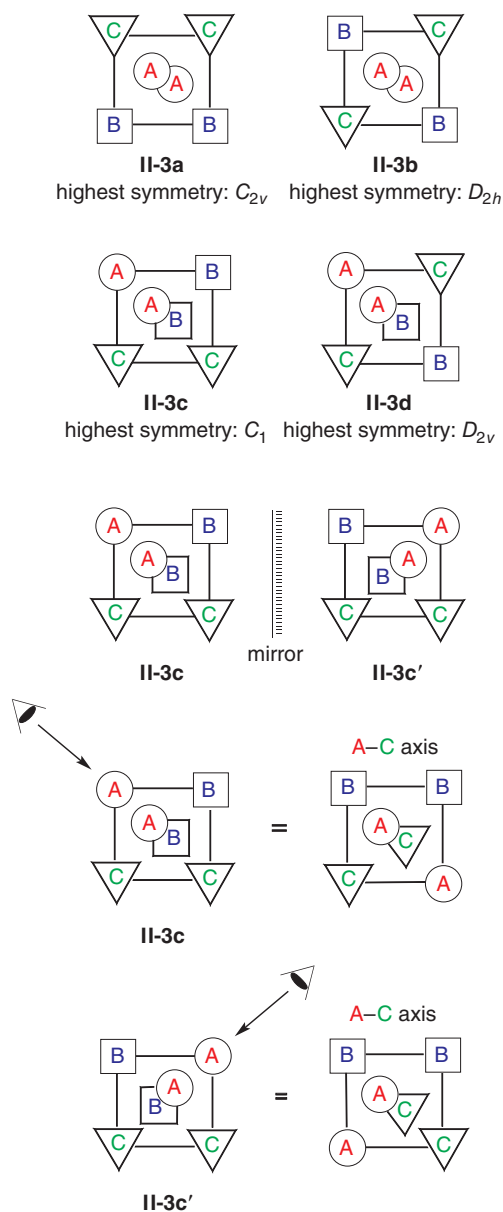


Figure 6. Tris-heteroleptic complexes: 2A-2B-2C.

### Through an A-A Axis

Two possibilities appear in the equatorial plane: in the first one (Figure 6), the two homoleptic ligands (B or C) are in cis positions (representation II-3a) or they are in trans positions (representation II-3b).

### Through an A-B Axis

With these new examples, the game becomes more complex, because it is necessary to look carefully at the molecules through different angles. The second ligand A should be in the equatorial position cis to the second ligand B (representation II-3c, Figure 6) or trans to it (representation II-3d).

The presence of a symmetry plane in II-3d makes it achiral. Structure II-3c is chiral because it is not superimposable on its mirror image. Compounds II-3c and II-3c' are thus enantiomers.

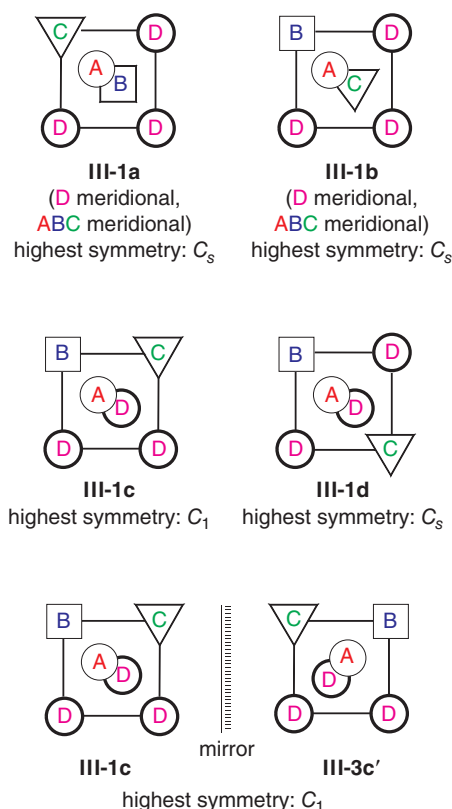


Figure 7. Tetakis-heteroleptic complexes: 1A-1B-1C-3D.

### Through an A-C Axis

With this last family, the different possibilities have all been illustrated in previous sections. The reason for this is that our general approach never precisely indicated the exact nature of B and C, so they are interchangeable. To confirm this fact, let us look at II-3c and II-3c' (Figure 6) through a different angle, using an A-C axis (it should be noted that II-3d does not possess any trans A-C axis and should therefore not be considered).

A total of five stereoisomers, three diastereoisomers (II-3a, II-3b, and II-3d) and one pair of enantiomers (II-3c and II-3c') is thus obtained for tris-heteroleptic complexes. An early example (1) of a  $[M(A)_2(B)_2(C)_2]$  type complex is  $[Pt(NH_3)_2(py)_2(Cl)_2]^{2+}$ . Shibata et al. (2) have resolved two purely inorganic tris-heteroleptic complexes into the enantiomeric forms: *cis,cis,cis*- $[Co(NH_3)_2(OH_2)_2(CN)_2]^+$  and *cis,cis,cis*- $[Co(NH_3)_2(OH_2)_2(NO_2)_2]^+$ .

These complexes are particularly interesting because if two of the monodentate ligands (A, B, or C) are attached to each other (e.g., diaminoalkanes), the compounds belong to the well-documented bidentate complexes.

### Tetakis-Heteroleptic Complexes

There are two possible octahedral complexes with four different monodentate ligands A, B, C, and D:  $[M(A)(B)(C)(D)_3]$  and  $[M(A)(B)(C)_2(D)_2]$ .

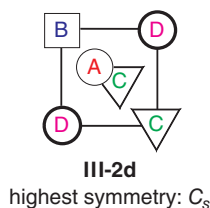
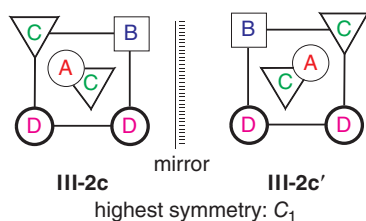
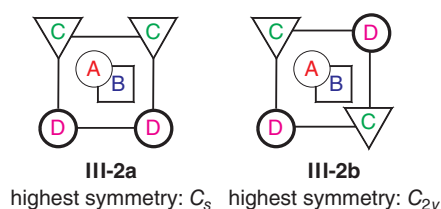


Figure 8. Tetrakis-heteroleptic complexes: 1A-1B-2C-2D.

### One Ligand A, One Ligand B, One Ligand C, Three Ligands D

Once again, we have chosen to observe the structures with ligand A in the axial position. Consequently, three families can be detailed, along an A-B axis, an A-C axis, and an A-D axis.

#### Through an A-B Axis or an A-C Axis

These two examples (Figure 7) can be studied together because the exact natures of B and C have not been defined, so they can be readily interchanged in our general approach. An A-B axis places B in the trans position relative to A, then C occupies the site in the equatorial plane (representation III-1a), the same thing happens in the case of an A-C axis (representation III-1b).

#### Through an A-D Axis

When the ligand D is placed trans to A, the problem can be simplified by considering the relative positions of the two remaining ligands D (Figure 7). They are necessarily in the equatorial plane in cis position (representation III-1c), or in trans position (representation III-1d). Please note that this discussion is very similar to cases II-3c and II-3d.

III-1d is achiral because of a symmetry plane. In the case of III-1c, which is not superimposable on its mirror image III-1c', this complex is a chiral structure (Figure 7).

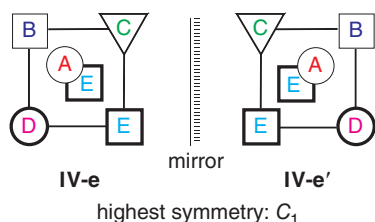
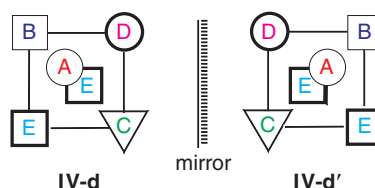
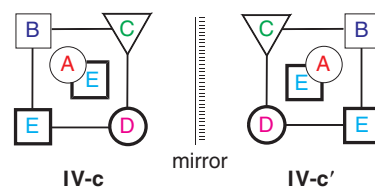
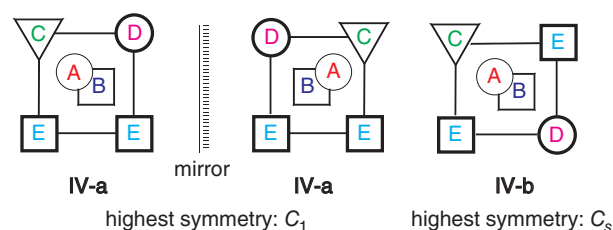


Figure 9. Pentakis-heteroleptic complexes: 1A-1B-1C-1D-2E.

### One Ligand A, One Ligand B, Two Ligands C, Two Ligands D

Three general possibilities need to be considered, along an A-B axis, an A-C axis, and an A-D axis.

#### Through an A-B Axis

When the ligand B is placed trans to A, the problem can be simplified by considering the relative positions of the four remaining ligands (two C and two D, Figure 8). The two ligands C can be cis to each other (representation III-2a) or trans to each other (representation III-2b).

#### Through an A-C Axis and an A-D Axis

Those two examples can be studied together because the exact natures of C and D have not been given, so they can be readily interchanged in our general approach. An A-C axis places C in the opposite position relative to A, with the remaining B, C, and two ligands D occupying equatorial positions (Figure 8). If the two ligands D occupy adjacent positions, we can draw the chiral structure III-2c (with its enantiomer III-2c') and if the

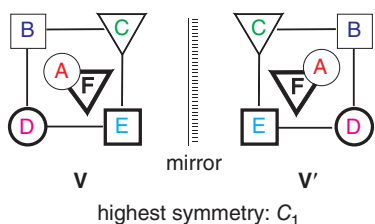


Figure 10. Hexakis-heteroleptic complexes: 1A-1B-2C-1D-1E-1F.

Table 1. Diastereoisomers of  $[\text{Pt}(\text{Br})(\text{Cl})(\text{I})(\text{NH}_3)(\text{NO}_2)(\text{py})]$ 

Diastereoisomers	Axial Ligands	Equatorial Plane	
1	$\text{NO}_2/\text{I}$	$\text{Cl}/\text{NH}_3$	$\text{Py}/\text{Br}$
2	$\text{Br}/\text{I}$	$\text{NO}_2/\text{NH}_3$	$\text{Py}/\text{Cl}$
3	$\text{Br}/\text{I}$	$\text{Py}/\text{NH}_3$	$\text{Cl}/\text{NO}_2$
4	$\text{Cl}/\text{I}$	$\text{Br}/\text{NH}_3$	$\text{Py}/\text{NO}_2$
5	$\text{Br}/\text{I}$	$\text{Py}/\text{NH}_3$	$\text{NO}_2/\text{Cl}$
V	A/F	B/C	D/E

NOTE: The last row refers to Figure 10.

two ligands **D** occupy trans positions, **III-2d** is achiral because of a symmetry plane.

### Pentakis-Heteroleptic Complexes

There is only one isomer of an octahedral complex with five different monodentate ligands **A**, **B**, **C**, **D**, and **E**:  $[\text{M}(\text{A})(\text{B})(\text{C})(\text{D})(\text{E})_2]$ .

One Ligand **A**, One Ligand **B**, One Ligand **C**,  
One Ligand **D**, Two Ligands **E**

At first, this case might seem to be more complex, but, in fact, assignment of **A**, **B**, **C**, and **D** are relative, so only two general cases need to be discussed. The first one is where a monodentate ligand, **B** for example, is trans to **A** in the axial position, and the second one is where **E** is trans to **A** in the axial position.

#### Through an A-B Axis

When the ligand **B** is placed trans to **A**, the problem can be simplified by considering the relative positions of the two ligands **E**. They can be adjacent to each other (structure **IV-a**, Figure 9) or opposite to each other (structure **IV-b**). Structure **IV-b** is achiral because of symmetry plane, whereas structure **IV-a**, without the presence of symmetry planes, is chiral, thus forming a pair of enantiomers with its nonsuperimposable mirror-image **IV-a'**.

#### Through an A-E Axis

When the ligand **E** is placed trans to **A**, ligand **B** can be placed arbitrarily on the top left corner with the following possible variations. Three enantiomeric couples will appear (Figure 9), completing our collection of chiral octahedral complexes (couples **IV-c** and **IV-c'**, **IV-d** and **IV-d'**, **IV-e** and **IV-e'**):

### Hexakis-Heteroleptic Complexes

There is only one isomer of an octahedral complex with six different monodentate ligands **A**, **B**, **C**, **D**, **E**, and **F**:  $[\text{M}(\text{A})(\text{B})(\text{C})(\text{D})(\text{E})(\text{F})]$ . After coming this far, you probably think the last case should be a nightmare, as all the ligands can be interchanged, five possible axes exist (an **A-B** axis, **A-C** axis, an **A-D** axis, an **A-E** axis, and an **A-F** axis). In fact, each case is the same and three enantiomeric couples can be drawn, giving fifteen pair of enantiomers (representations **V** and **V'**) or a total of 30 stereoisomers (Figure 10).

Essen et al. (3–5) synthesized five diastereoisomers of one hexakis-heteroleptic complex  $[\text{Pt}(\text{Br})(\text{Cl})(\text{I})(\text{NH}_3)(\text{NO}_2)(\text{py})]$ . These different diastereoisomers are given in Table 1, according to the Newman projection described in structure **V**.

### Conclusion

Enumeration of all the possible diastereoisomers of octahedral complexes with monodentate ligands yields a total of 75 stereoisomers, which can be classified into five families. Historically, the Bailar table (6) has allowed an exhaustive determination of all the different diastereoisomers for each family. We think this earlier approach is difficult to explain and understand as experienced in the course of our teaching activities at the Master level. With the method that we present here, it is much easier to see which stereoisomers possess chirality.

It is impossible to imagine, in light of this exhaustive presentation, that octahedral complexes in transition-metal chemistry cannot be responsible for asymmetric induction!

### Acknowledgment

We would like to thank K. Plé for helpful discussions.

### Note

1. Ligands **A**, **B**, **C**, **D**, **E**, and **F** are indicated in color in the online version of the manuscript.

### Literature Cited

- Kauffman, G. B. *Inorganic Coordination Compounds*; Heyden & Son, Ltd.: London, 1981.
- Ito, T.; Shibata, M. *Inorg. Chem.* 1977, 16, 108–115.
- Essen, L. N.; Gelman, A. D. *Zh. Neorg. Khim.* 1956, 1, 2475–2487.
- Essen, L. N.; Zakharova, F. A.; Gelman, A. D. *Zh. Neorg. Khim.* 1958, 3, 2654–2661.
- Essen, L. N.; Bukhtiyarova, T. N. *Zh. Neorg. Khim.* 1967, 12, 1405–1406.
- Bailar J. C., Jr. *J. Chem. Educ.* 1957, 34, 334.

### Supporting JCE Online Material

<http://www.jce.divched.org/Journal/Issues/2008/Mar/abs436.html>

Abstract and keywords

Full text (PDF)

Links to cited JCE articles

Color figures